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A QUARTERLY JOURNAL OF FUEL SCIENCE

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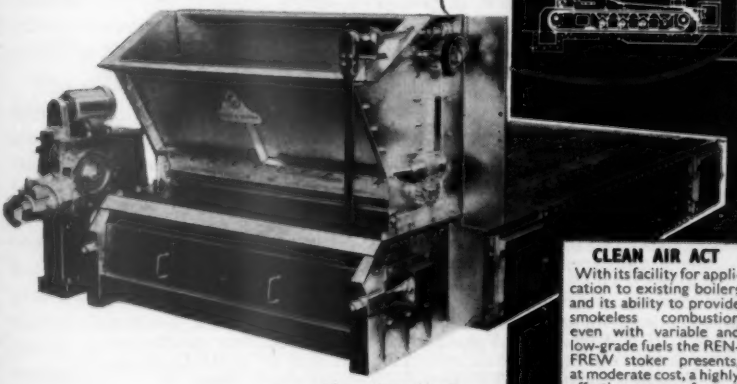

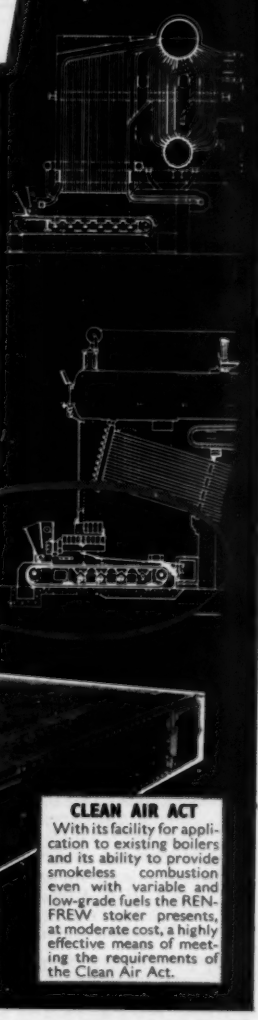

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BUTTERWORTHS SCIENTIFIC PUBLICATIONS

The Dependence of the Elastic Behaviour of Coal on the Microcrack Structure

N. B. TERRY

Some laboratory investigations into the physical structure of coal, using acoustic techniques, are described. The elastic wave velocity perpendicular to the bedding plane is shown to be markedly dependent upon external stress for the four British coals examined. These results together with the results of experiments involving the impregnation of coal with water and a crystalline cement, of experiments on models consisting of piles of thin plates and of a microscopic examination of coal, are evidence of a system of microscopic cracks, of thicknesses of the order of 10 microns, probably flat in shape and oriented with their flat surfaces parallel to the bedding planes. Thus for these coals, it is the microcrack structure, rather than any low crystallinity, that is responsible for the transversely isotropic elastic symmetry observed.

COAL has a stratified structure, consisting of layers of macroscopic components such as vitrain, durain, clarain and fusain, which differ in their physical and chemical properties and occur in planes parallel to the bedding plane. There is a macroscopic crack structure, known as the main cleating, the planes of the cracks being oriented at about 90° to the bedding plane, and often a further set of cleat planes, known as the cross cleating, which for the coals considered here, is oriented approximately perpendicularly to both the main cleating and the bedding plane. Irregular macroscopic cracks can also be observed in most samples of coal, and there is considerable evidence that coal is highly porous[1], the size of the pores ranging down to a few Ångström units.

The elastic properties of several coals have been investigated in these laboratories using both static and dynamic techniques[2,3]. Static measurements[2], involving the compression of cubes or the bending of thin strips of coal, have shown that for most of the specimens tested, a linear relationship between the applied and the resulting strain is obtained, although initially there is some non-linearity due to the deformation of cracks. For most static tests carried out in these laboratories, no significant differences in the moduli have been obtained between tests in which the stresses were applied parallel and those in which the stresses were applied perpendicular to the bedding planes; however, the scatter between samples is fairly large, undoubtedly owing to the effects of macroscopic cracks, so that small differences in the moduli for the different orientations would always be difficult to detect.

One dynamic technique[2] involved the vibration of small cylinders of coal; by measuring the longitudinal and torsional resonance frequencies, the velocities of longitudinal and torsional elastic waves along the lengths of the specimen were calculated. The appropriate elastic modulus k is given by

$$c^2\rho = k \qquad \ldots . [1]$$

where c is the elastic wave velocity and ρ is the density. For Barnsley Hards (a strong bituminous coal) and Pumpquart anthracite, the samples measured

were two or three centimetres in length and had been selected so as to be free of macroscopic cracks. The measurements obtained showed a low 'between sample' scatter and the coals were found to be transversely isotropic, i.e. the elastic properties were symmetrical about an axis perpendicular to the bedding plane. The elastic moduli measured in the direction of the axis of symmetry were lower than those measured in the direction perpendicular to the axis. *Table 1* gives a summary of the results obtained.

Table 1. Summary of dynamic resonance measurements on small samples of Barnsley Hards and Pumpquart anthracite

Coal	*Orientation of cylinder axis with reference to bedding plane*	*Experimental modulus dyne/cm²*	*Standard error of the mean dyne/cm²*
Barnsley Hards	*Parallel*	*Young's* $E_{\parallel}$ 4·03 × 10^{10}	0·05 × 10^{10}
	Perpendicular	*Young's* $E_{\perp}$ 3·27	0·08
	Parallel	*Rigidity* $G_{\parallel}$ 1·36	0·03
	Perpendicular	*Rigidity* $G_{\perp}$ 1·18	0·02
Pumpquart anthracite	*Parallel*	*Young's* $E_{\parallel}$ 5·42 × 10^{10}	0·07 × 10^{10}
	Perpendicular	*Young's* $E_{\perp}$ 4·59	0·08
	Parallel	*Rigidity* $G_{\parallel}$ 1·65	0·03
	Perpendicular	*Rigidity* $G_{\perp}$ 1·47	0·05

The other dynamic technique[3] used consisted of measuring the velocities of compressional elastic pulses transmitted through blocks of coal of up to 30 cm in length; since this technique has also been used for the present series of experiments, a brief description of the apparatus will be given later. Measurements made on Barnsley Hards and Barnsley Brights coals gave evidence of transverse isotropy.

J. SCHUYER, H. DIJKSTRA and D. W. VAN KREVELEN[4], using a very high frequency elastic pulse technique, have made measurements of the elastic wave velocities in small samples of different vitrains and have derived the elastic moduli by using equation 1. Their results showed that those vitrains having a carbon content higher than 93 per cent were transversely isotropic; for lower carbon contents the vitrains were isotropic.

In a previous publication[2], several possible explanations of the transversely isotropic behaviour observed in coal have been suggested; these are discussed below.

(*a*) There might be an anisotropy in the binding forces between particles or molecules in the basic coal substance. Now although x-ray analysis has shown some evidence of low crystallinity in vitrains[5], the degree of crystallinity increasing with rank, the elastic measurements of *Table 1* indicate that the low rank Barnsley Hards coal exhibits as marked an elastic anisotropy as the high rank anthracite. Thus it seems unlikely that the anisotropy observed can be completely explained in this way.

(*b*) There might be differences in the elastic properties of the component layers, i.e. vitrain, durain, clarain and fusain. It may be shown[2], in fact, that a

layered body will exhibit transverse isotropy even if the components are isotropic. The degree of transverse isotropy depends upon the layers. However, fairly large differences are required to account for the degree of anisotropy observed. For example, for Barnsley Hards coal it may be shown, using the appropriate relationship derived by W. T. A. MORGANS and N. B. TERRY[2], that the moduli of bright and dull coal components would have to be in the ratio of about two or three to one (or vice versa) to account for the anisotropy evident from the results of *Table 1*. The few experiments which have been carried out to determine the elastic properties of the various dull and bright component layers have not shown such large differences[6].

(*c*) The formation of coal as a layered material could have resulted in a crack distribution having a preferred orientation (apart from the main and cross cleating). It can readily be seen, for example, that a number of flat cavities, situated in the plane of the layers, could give rise to a transversely isotropic symmetry (see *Figure 1*—for ease of reference these cavities are referred to as the 'layer cavities').

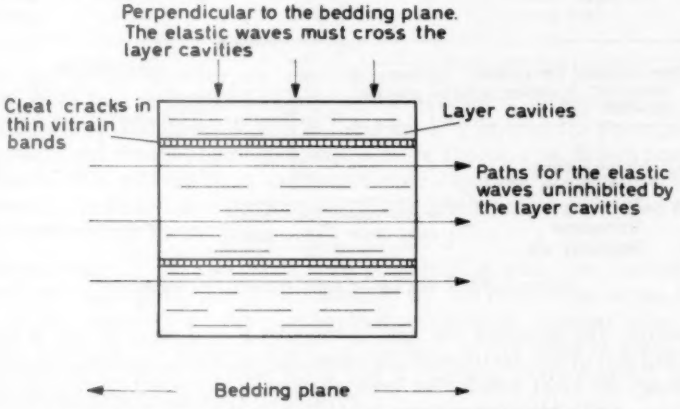
Perpendicular to the bedding plane. The elastic waves must cross the layer cavities
Cleat cracks in thin vitrain bands
Layer cavities
Paths for the elastic waves uninhibited by the layer cavities
Bedding plane

Figure 1. Suggested microcrack orientations in Barnsley Hards coal

Since of the possible explanations advanced, those under *a* and *b* are not sufficient in themselves to account for all the anisotropy, serious attention must be given to the hypothesis *c*. The present paper describes some acoustic experiments to investigate the nature of the crack structure in coal.

EXPERIMENTAL METHOD

Introduction—Acoustic techniques are admirably suited for these investigations since the cracks may be assumed to contain air (or possibly methane for cracks having no outlet to the atmosphere), and the elastic wave velocity in dry air (at n.t.p.) of 0·331 km/s is about an order lower than that in coal ($\simeq$ 2 km/s). Normal flaw detection techniques, which involve the reflection of acoustic waves from cracks and other discontinuities, cannot, however, be used. This is because the attenuation in coal increases rapidly with frequency[7]; thus only wavelengths much longer than the width of the cracks

encountered can in practice be detected after transmission into the specimens so that detectable reflections from the cracks are not obtained. However, the transit time of an elastic wave across a sample of coal may be considered to consist of two components, namely the transit time in the coal substance itself and the transit time across the gas-filled cracks. If external stresses are applied to the coal sample, some of the cracks may be expected to close, thus reducing the air path of elastic waves transmitted in the direction of the applied stress, and reducing the overall transit time. By investigating the decrease of transit time (or increase of wave velocity) with increasing external stress, for different orientations of applied stress with respect to the bedding and cleat planes, information about the orientation of cracks in the specimen can be obtained.

Description of apparatus—Since this has been given in detail elsewhere[3], only a brief consideration will be given here. *Figure 2* shows a block diagram of the

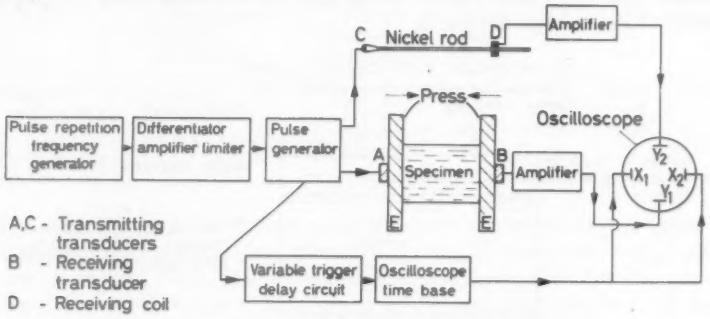

Figure 2. Block diagram of pulse transmission apparatus

apparatus. The specimen was held in the jaws E of a press. A and B were a matched pair of barium titanate electromechanical transducer discs (resonance frequency 90 kc/s) which had been electrically polarized in the thickness direction, and which were spring loaded on to the jaws E. C was a barium titanate transducer (resonance frequency 200 kc/s) held in contact with one end of a $\frac{3}{16}$ in. diameter magnetically polarized nickel rod, and D was a small coil (value 1 mH) mounted concentrically about the nickel rod and adjustable in position along it.

The pulse generator impressed a high voltage pulse (1 080 V at a repetition rate of 25 c/s) across the faces of the transducers A and C (these were connected in parallel), thereby shock exciting these transducers into mechanical vibration. Longitudinal elastic pulses were thus simultaneously generated into the specimen and nickel rod; the pulse traversing the specimen was detected by the transducer B, amplified and displayed on one beam of a cathode ray oscilloscope, whilst that travelling along the nickel rod was detected magnetostrictively by the coil D, amplified and displayed on the other beam of the oscilloscope. By adjusting the position of the coil D until the two received pulses were accurately aligned, the transit time through the specimen and the jaws of the press could be obtained by measuring the length

of nickel rod between C and D; the transit time per unit length of the nickel rod had previously been determined. Transit time through the specimen was obtained by applying a correction for transit time through the jaws of the press. For all measurements thin films of a paste of kaolin clay–glycerine were applied to the appropriate interfaces to ensure good acoustic contact.

EXPERIMENTAL RESULTS ON UNTREATED COALS

Descriptions of coal samples—The measurements were carried out on the coals listed in *Table 2*.

Table 2

Colliery	*Seam*	*N.C.B. Coal Rank Code No.*	*Approximate volatile matter, %*	*Description*
Rossington	*Barnsley (Top Hards)*	801	34	*Very strong, dull coal*
Pentremawr	*Pumpquart*	100a	7	*Anthracite*
Cwmtillery	*Garw*	301/501	28	*Friable, weak coal*
Pleasley	*Dunsil*	7/802	43	*Strong coal*

All the specimens were cut into rectangular prisms of approximately square cross section by using high speed carborundum slitting wheels. The Barnsley Hards specimens were 3 in. × ¾ in. × ¾ in. and the Pentremawr, Cwmtillery and Pleasley specimens were 3 in. × 1 in. × 1 in. Where possible specimens were selected so as to contain as few random macroscopic flaws as possible; however, only the Barnsley Hards specimens could be said to be free of obvious cracks and flaws.

Three groups of ten specimens were prepared for each coal (except the anthracite), each group being characterized by the orientation of the long axis of the prism. The three orthogonal orientations selected were: (*a*) perpendicular to the bedding plane, (*b*) parallel to the bedding plane and perpendicular to the cross cleat plane and (*c*) parallel to the bedding plane and perpendicular to the main cleat plane.

For the Pumpquart anthracite, it was difficult to obtain lumps showing consistent cleat directions, so specimens cut parallel to the bedding plane were not cut with any specific orientation with respect to the cleat planes.

Experimental procedure—The elastic wave velocities were measured in the same direction as the applied external stress. Each specimen was subjected to a discrete number of stress levels ranging from zero stress to either the stress corresponding to the limit of the press or to the failure stress of the specimen; transit times were measured at each stress level. Changes in the length under stress were less than 1 per cent and were neglected in the calculation of wave velocities.

The attenuation characteristics of coal depend on the disposition of cracks and therefore on any changes in crack shape due to an applied external stress; thus the shape of the pulse received after transit is stress dependent. However, in this work, the leading edge of the pulse was used to define the pulse position and it was found that in general the leading edge was sharply defined; thus

it was considered that no serious errors in the estimation of pulse velocity were caused by the variation of attenuation with stress.

For some specimens the strains perpendicular to the bedding planes were measured (using a roller-type extensometer in the manner previously described[2]) as well as the elastic wave velocities. Specimens were tested in the air-dried state under room conditions.

Typical curves for each of the four coals tested are shown in *Figures 3, 4, 5* and *6*. The velocity/stress curves have not been corrected for the effect of

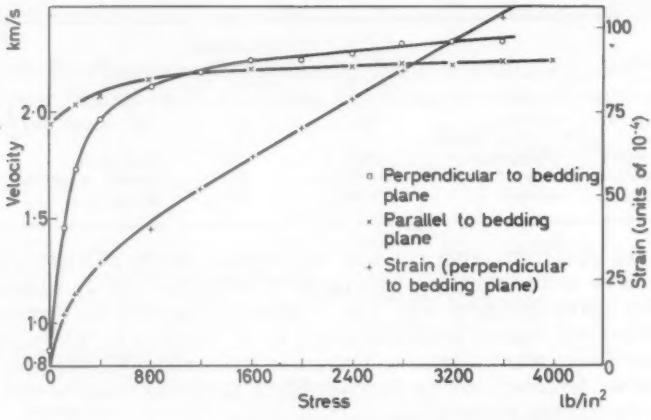

Figure 3. Variation of elastic wave velocity and strain with stress for Barnsley Hards coal

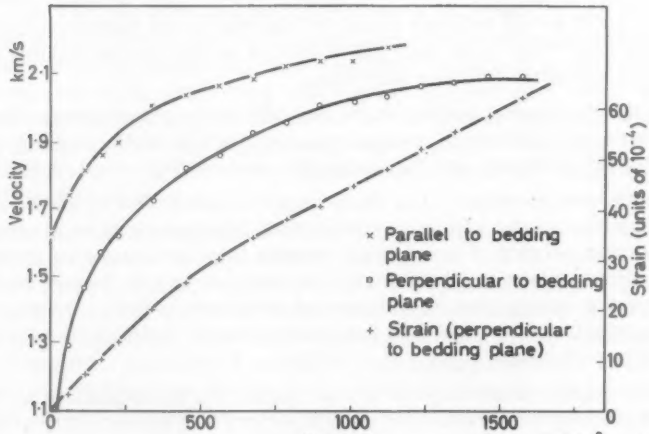

Figure 4. Variation of elastic wave velocity and strain with stress for Pumpquart anthracite coal

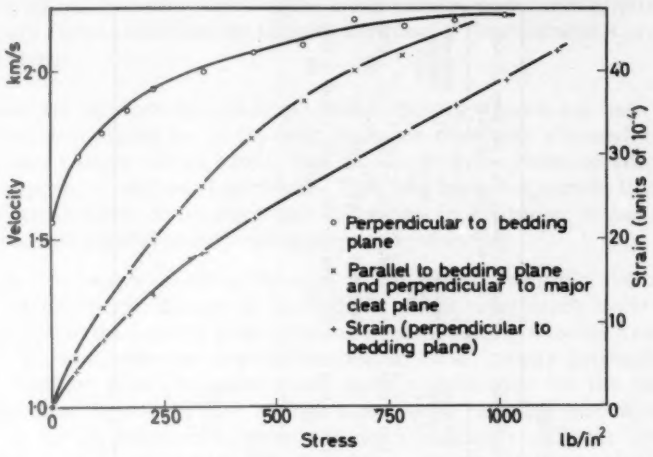

Figure 5. Variation of elastic wave velocity and strain with stress for Cwmtillery coal

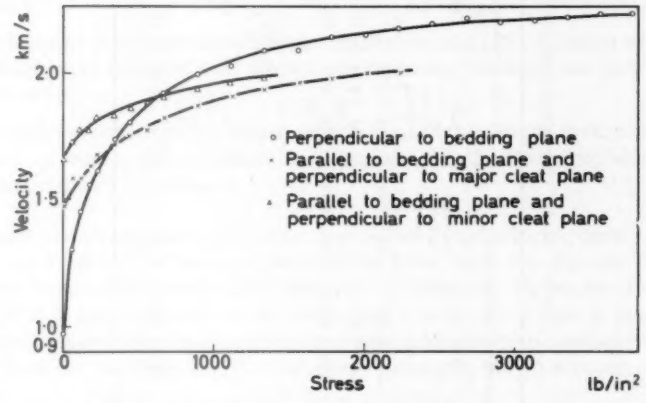

Figure 6. Variation of elastic wave velocity with stress for Pleasley coal

bedding down between the specimen and the surfaces of the press; but experiments showed that, provided the end surfaces of the specimens are reasonably plane, the effect is negligible.

In *Table 3* the results of measurements for the different coals are given. These include, for all orientations, the velocities at zero stress, the velocities at a high stress level S (S was the highest stress level sustained without rupture by the majority of the specimens of a particular coal) and in the case of Barnsley Hards and Pleasley coals, where a linear relationship between velocity and stress was obtained at the high stresses, the 'intercept velocities', i.e. the intercepts of the linear portions of the velocity/stress curves on the

Table 3. Elastic wave velocities at high and low stresses

Coal	Stress S lb/in²	Perpendicular to bedding plane			Parallel to bedding plane and perpendicular to cross cleat plane			Parallel to bedding plane and perpendicular to the main cleat plane		
		Velocity at zero stress km/s	Velocity at stress S km/s	Intercept velocity km/s	Velocity at zero stress km/s	Velocity at stress S km/s	Intercept velocity km/s	Velocity at zero stress km/s	Velocity at stress S km/s	Intercept velocity km/s
Barnsley Hards	1600	1·30 ± 0·07	2·11 ± 0·02	2·16 ± 0·03	2·04 ± 0·04	2·17 ± 0·03	2·13 ± 0·04	1·98 ± 0·04 (9)	2·20 ± 0·02 (9)	2·16 ± 0·02 (6)
Cwmtillery	780	1·47 ± 0·09	2·07 ± 0·03	—	1·03 ± 0·04 (8)	1·94 ± 0·03 (6)	—	1·08 ± 0·05	1·88 ± 0·04	—
Pleasley	1340	1·00 ± 0·03	2·09 ± 0·02	2·11 ± 0·03	1·68 ± 0·05 (9)	2·02 ± 0·04 (8)	1·93 ± 0·03 (9)	1·31 ± 0·14 (6)	1·95 ± 0·05 (5)	1·83 ± 0·10 (6)
					Parallel to bedding plane (no cleat direction specified)					
					Velocity at zero stress km/s	*Velocity at stress S km/s*	*Intercept velocity km/s*			
Anthracite	760	1·10 ± 0·06	1·88 ± 0·04 (8)	—	1·43 ± 0·06	2·07 ± 0·03 (4)	—			

velocity axes. The data in the *Table 3* are the means and standard errors of the means; where less than ten samples were tested, their number is given in parentheses.

Results for the Barnsley Hards specimens—Barnsley Hards has both main and cross cleat planes, but as the cleat cracks are often widely spaced, except in the very narrow vitrain bands, they would not be expected to affect the measurements to any marked degree. That this is so is apparent from results given in *Table 3*; no important differences in behaviour between the two directions parallel to the bedding plane were observed.

In the unstressed condition the coal is transversely isotropic, the elastic wave velocity perpendicular to the bedding plane being much lower than that parallel to the bedding plane (this confirms the results of earlier measurements[2, 3]). As stresses are applied, the elastic wave velocity perpendicular to the bedding plane increases much more rapidly than for the parallel direction (see *Figure 3*) until at high stresses the intercept velocities (see *Table 3*) for all three orientations are not significantly different. For all orientations, the velocity/stress curves become linear at high stress levels. If, as seems likely, the initial rapid increase of velocity with stress is due to the closing of cracks, then the intercept velocity is a rough measure of the wave velocity which would be obtained at zero stress if these cracks were absent.

The measurements were found to be repeatable even after repeated stressing and de-stressing provided that the specimen was not stressed too near to its rupture stress.

The results show Barnsley Hards to be a coal for which the anisotropy is a function of stress; the symmetry is dependent on the reversible structural changes produced by stressing.

Results for Pumpquart anthracite specimens—The velocity/stress curves shown in *Figure 4* for the anthracite differ from those for Barnsley Hards in that a linear relationship is not obtained. Considering the results shown in *Table 3*, it is apparent that in the unstressed condition the coal is markedly transversely isotropic; this confirms the results of previous measurements[2]. At high stress, the coal is still transversely isotropic, but to a much smaller degree.

Results for Cwmtillery specimens—This coal has two cleat planes, approximately perpendicular to each other, the cleat cracks in each case being finely spaced (approximately $\frac{1}{8}$ in. apart). It is, in fact, difficult to distinguish between the main and cross cleats except on the large rough blocks. The coal specimens used contained a regular network of macroscopic cleat cracks in addition to random cracks and flaws. It would be expected, therefore, that for this coal the effect of cleat would be important and that this is so is illustrated by the results obtained.

The results shown in *Table 3* are quite different from those for the other coals tested in that, although the coal is transversely isotropic at zero stress, the elastic wave velocity perpendicular to the bedding plane is significantly

higher than that for the other two directions. This is undoubtedly due to the effect of the cleat cracks in reducing the velocity for the two directions parallel to the bedding plane. At high stresses, the differences in the velocities for the perpendicular and parallel orientations are much less than at zero stress (see *Table 3* and *Figure 5*).

Results for Pleasley specimens—Pleasley coal possesses two cleat planes, approximately perpendicular to each other. The main cleat planes are finely spaced (approximately $\frac{1}{4}$ in. to $\frac{1}{2}$ in. between cracks) whereas the cross cleat planes are more sparsely distributed, being sometimes as much as 2 or 3 in. apart.

The results given in *Table 3* show that at zero applied stress, the coal exhibits orthorhombic symmetry with respect to the elastic wave velocity, the velocities for all three orientations being significantly different from each other.

The curves shown in *Figure 6*, as well as the results given in *Table 3*, show that the velocity perpendicular to the bedding plane increases considerably with increasing applied stress; the increase of the velocity perpendicular to the main cleat is less but is still considerable, whereas the velocity perpendicular to the cross cleat undergoes only a small increase with increasing stress.

It is clear from the results shown in *Table 3* that the fractional differences between the elastic wave velocities corresponding to the different orientations are considerably less in the highly stressed than in the unstressed condition.

General considerations of the results

The effect of the cleat cracks on the elastic wave velocities are clearly demonstrated by the results for Cwmtillery and Pleasley coals, the only coals tested which have a marked cleating. The large increase in elastic wave velocity with stress for an orientation perpendicular to a finely spaced cleating is simply explained by the closing, or partial closing, of the cleat cracks.

For all coals, however, a very large increase in elastic wave velocity with increased stress was obtained for the orientation perpendicular to the bedding plane and it is difficult to escape from the conclusion that this is due to the closing of flat cracks which are oriented with their flat surfaces parallel to the bedding plane, i.e. the layer cavities.

Figures 3, *4* and *5*, for Barnsley Hards, Pumpquart anthracite and Cwmtillery specimens show that near the origin the stress/strain curves are initially concave downwards and at higher stresses become straight lines, the slopes of which are measures of the inverse Young's moduli. It has previously been pointed out[2] that the intercepts of the linear portions of the stress/strain curves on the strain axes (the 'strain intercepts') give a rough measure of the cracks closed or partially closed during compression. It was shown that for Barnsley Hards and Pumpquart anthracite, the strain intercepts were significantly larger for stresses applied perpendicular to the bedding plane than for stresses applied parallel to the bedding plane[2]; for Cwmtillery the reverse applies[8]. These results are consistent with the deductions from the results

of the present work; the strain intercepts measured for the Barnsley Hards and Pumpquart anthracite specimens are larger for the perpendicular orientation because of the closing of the layer cavities, whereas for Cwmtillery the extensive cleating accounts for the large strain intercept obtained by stressing parallel to the bedding plane.

It can be seen from *Figures 3*, *4* and *5* that, for the perpendicular orientation, the elastic wave velocity continues to increase slightly over the range of stresses corresponding to the linear portion of the stress/strain curves (similar results were obtained when stresses were applied parallel to the bedding plane). This would be an apparent contradiction for a homogeneous material, since a linear stress/strain curve indicates that the elastic modulus is independent of stress, whereas, from equation 1, a stress-independent modulus should mean that the wave velocity is also independent of stress (neglecting changes due to the slight increases of density under stress). The paradox is resolved if it is assumed that some of the cracks have not completely closed, even at stresses corresponding to the linear portion of the stress/strain curve, but continue to close elastically under increasing stress thereby reducing the gaseous path and resulting in an increase of elastic wave velocity. It follows that one important difference between static and dynamic tests of the elasticity of coal is that for the static tests, a high external load is applied to the sample so that the cracks are in a closed or partially closed condition; in the usual type of dynamic test (see refs 2 to 4), however, only the very low alternating stresses of the elastic wave are applied and the cracks are not closed. Thus it would be expected that a more marked anisotropy would be observed by dynamic testing; unfortunately the 'between sample' scatter for the static tests is often too large to detect the anisotropy at all.

SOME IMPREGNATION EXPERIMENTS WITH BARNSLEY HARDS COAL

If, as has been suggested, the elastic anisotropy of coal is due to an orientation of cavities containing air, it follows that, if the air can be removed and replaced by a liquid or solid, changes in the anisotropy should result. This is to say, changing the pore-filling medium from one having a low elastic wave velocity to one having a comparatively high elastic wave velocity, should increase considerably the overall velocity for directions in which the cavity path is large. Several such impregnation experiments were carried out.

Impregnation with water—Since the elastic wave velocity in water $\simeq$ 1·5 km/s (at n.t.p.), i.e. some five times that in air, water impregnation of coal should be expected to change the acoustic properties.

It was found, however, that the results obtained for groups of Barnsley Hards specimens soaked in water for 450 hours were not significantly different from those obtained for unsoaked specimens of the same coal. Evidently any changes in the anisotropy due to soaking are so small as to be masked by the 'between sample' variation. It was concluded that this was due to the fact that the water was unable to penetrate completely into the cracks because the air contained in these was unable to escape. Evidently evacuation is required prior to soaking in order to obtain a thorough impregnation.

The velocity/stress curve for a Barnsley Hards specimen, $\frac{3}{4}$ in. $\times$ $\frac{3}{4}$ in. $\times$ 3 in. oriented perpendicular to the bedding plane, was measured in the

usual air-dried condition. The specimen was then placed in a flask, and the flask was evacuated to a pressure of 0·05 mm of mercury; 1½ h after the evacuation had commenced water was introduced to cover the specimen (without allowing air to enter), which was then soaked for 1 h. After soaking, the velocity/stress curve was re-measured. The specimen was again placed in an evacuated flask, this time for 144 h, then soaked for 216 h, and the velocity/stress curve again re-measured. *Figure 7* shows the curves obtained.

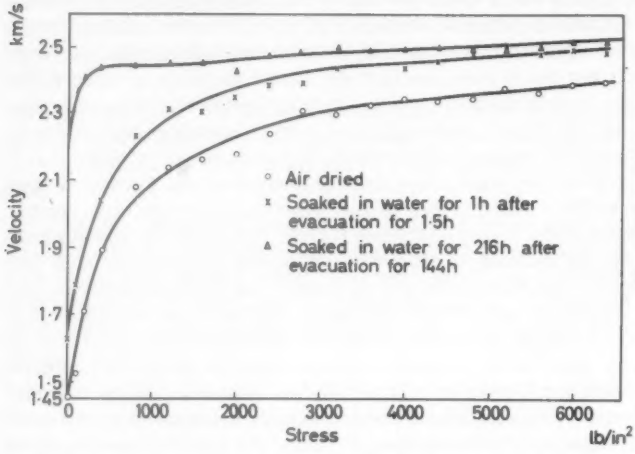

Figure 7. Effect of water impregnation on the variation of elastic wave velocity with stress (Barnsley Hards, stress perpendicular to bedding plane)

The curves show that, after the final soaking, the velocity at zero stress has increased considerably, and the overall increase of velocity obtained under stress has been considerably reduced. Further experiments were carried out on three more Barnsley Hards specimens, one oriented perpendicular and two oriented parallel to the bedding plane; in this case the velocity/stress curves for the specimens were measured first of all in the air-dry condition, and again after evacuation for 166 h and soaking for 240 h. *Table 4* shows, for all four specimens, the elastic wave velocities obtained at zero stress and at a stress of 3 500 lb/in² in both the air-dried and water-impregnated conditions. It is evident that the increase in the zero stress elastic wave velocity, due to the water impregnation, is much more marked for the perpendicular than for the parallel orientation. The increase in wave

Table 4. Elastic wave velocities at high and low stresses for Barnsley Hards specimens impregnated with water

Orientation of specimen with respect to bedding plane	*Air-dried condition*		*Water-impregnated condition*	
	Velocity at zero stress km/s	*Velocity at stress of 3500 lb/in² km/s*	*Velocity at zero stress km/s*	*Velocity at stress of 3500 lb/in² km/s*
Perpendicular	1·53	2·30	2·01	2·44
Perpendicular	1·45	2·28	2·19	2·48
Parallel	2·15	2·23	2·24	2·49
Parallel	2·03	2·18	2·41	2·45

velocity with stress, however, is considerably reduced by water impregnation for the perpendicular orientations, but little changed for the parallel orientation. These results give strong support to the layer cavity hypothesis.

Impregnation with phenyl salicylate (Salol)—This is a well known crystalline cement; the elastic pulse velocity through a polycrystalline rod of solid Salol was found to be 1·6 km/s. Since it has a low melting point (34°C) Salol was considered to be a suitable material for the solid impregnation of the coal. Two groups of Barnsley Hards specimens were prepared having perpendicular and parallel orientations and of dimensions ¾ in. × ¾ in. × 3 in. The elastic wave velocities along the long axes of the specimens, at zero stress and also at a stress of 200 lb/in² were first measured under room conditions in the air-dried state. The specimens were then placed in a vessel containing solid Salol, and the vessel placed in an unheated vacuum oven. After evacuation for 336 h to a pressure of 0·05 mm of mercury, the temperature of the oven was raised to 67°C so that the Salol melted, completely covering the specimens. The specimens were soaked for 12 h at this temperature, and then removed from the Salol. The surplus Salol was wiped off, and the specimens were left for a few days to allow the Salol to freeze completely. Velocity/stress curves for the specimens were then measured.

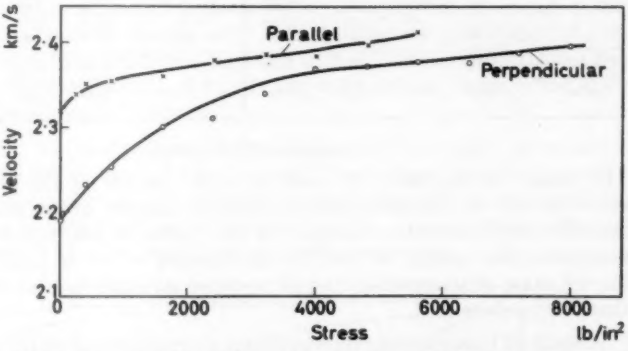

Figure 8. Variation of elastic wave velocity with stress for Barnsley Hards specimens impregnated with Salol

Typical velocity/stress curves for the two orientations of Salol-impregnated specimens are shown in *Figure 8*. It can be seen, comparing these curves with the velocity/stress curves for the unimpregnated specimens shown in *Figure 3*, that for both orientations the variation of velocity with stress has been considerably reduced, the reduction being greater for the perpendicular orientation. The detailed results obtained are given in *Table 5*.

Considering the mean velocities at zero stress, it can be seen from *Table 5* that the effect of impregnation is to increase the velocity in the perpendicular orientation by some 42 per cent compared with only 13 per cent for the parallel orientation. Moreover, for the unimpregnated specimens having the perpendicular orientation, increasing the stress from zero to 200 lb/in² increases the velocity by 29 per cent, but in the impregnated condition the corresponding increase in velocity is only 2 per cent; corresponding values for the parallel orientation are 4 per cent and 1 per cent.

Evidently these effects are due to the replacement of air in the layer cavities by solid Salol since Salol would prevent closing of the cavities under stress.

The experiments described above were repeated on two similar groups of specimens in exactly the same manner, except that the temperature of the oven was raised to only 50°C. The results obtained were very similar to those described above. Since changing the temperature of treatment from 67° to 50°C had no significant effect on the results, it is probable that little physical damage was sustained by the specimens solely because of the heating.

Table 5. Elastic wave velocities at high and low stresses for Barnsley Hards specimens impregnated with Salol

Perpendicular to bedding plane					*Parallel to bedding plane*				
	Before impregnation		*After impregnation*			*Before impregnation*		*After impregnation*	
Specimen	*Velocity at zero stress km/s*	*Velocity at stress of 200 lb/in² km/s*	*Velocity at zero stress km/s*	*Velocity at stress of 200 lb/in² km/s*	*Specimen*	*Velocity at zero stress km/s*	*Velocity at stress of 200 lb/in² km/s*	*Velocity at zero stress km/s*	*Velocity at stress of 200 lb/in² km/s*
1	1·47	1·94	2·22	2·25	*8*	1·93	2·15	2·45	2·46
2	1·58	1·98	2·19	2·21	*9*	2·18	2·21	2·40	2·42
3	1·58	2·00	2·13	2·15	*10*	2·09	2·17	2·42	2·42
4	1·53	1·99	2·20	2·22	*11*	2·09	2·19	2·35	2·37
5	1·41	1·92	2·07	2·18	*12*	2·16	2·18	2·37	2·39
6	1·53	1·97	2·13	2·19	*13*	2·12	2·16	2·26	2·41
7	1·56	1·94	2·19	2·20	*14*	2·14	2·18	2·32	2·34
Mean standard	1·52	1·96	2·16	2·20		2·10	2·18	2·37	2·40
Error of the mean	0·02	0·0	0·02	0·01		0·03	0·01	0·02	0·01

EXPERIMENTS ON MODELS

The structure suggested for coal from the results of the work described above is that of a layered material with flat cavities of macroscopic or submicroscopic thicknesses, situated in the plane of the layers. In order to determine the validity of this, it was decided to try to construct a model having these characteristics and to compare its experimental behaviour with that observed for coal.

A stack of thin ebonite plates provides a simple model of the type required; the plane of the plates corresponds to the bedding plane of the coal. Since, as a consequence of imperfections in the machining and of warping, the plates do not have exactly plane surfaces, there must be flat cavities situated between neighbouring plates in the stack.

For the first experiments, a 2 in. diameter ebonite rod was cut into two pieces. One piece was machined to a solid cylinder, $2\frac{1}{2}$ in. long, whereas the other piece was machined into 40 discs each $\frac{1}{16}$ in. thick. The velocity/stress curves shown in *Figure 9* were obtained by stressing the solid cylinder along its axis and also stressing the stack of 40 discs in the direction perpendicular to the plane of the discs. It can be seen that at low stresses, the wave velocity through the stack is much lower than that through the solid material, undoubtedly because of the effect of the cavities between the plates. Whereas, for the solid ebonite, the wave velocity has increased only slightly at high stress, a considerable increase in wave velocity was observed for the stack,

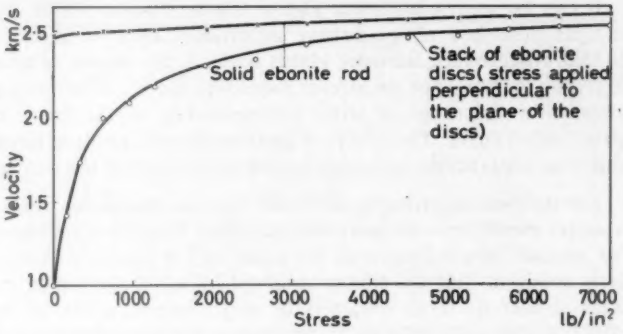

Figure 9. Variation of elastic wave velocity with stress for a stack of 40 ebonite discs ($\frac{1}{16}$ in. thick) and a solid ebonite rod

this being undoubtedly due to the closing of the cavities under compression; at high stress, the velocity for the stack is very nearly equal to that for the solid cylinder.

Further experiments were carried out on a model constructed of 32 square plates of ebonite, each of dimensions 4 in. × 4 in. × $\frac{1}{8}$ in. and all cut from the same ebonite sheet. The plates were stacked to form an approximate cube of side 4 in. and velocity/stress curves were measured for the directions perpendicular and parallel to the plane of the layers (when stressing in the parallel direction, two G clamps were used to hold the pile together and prevent buckling). The two curves, together with a stress/strain curve for the perpendicular direction (obtained by placing a dial gauge between the jaws of the press), are shown in *Figure 10*.

At zero stress, the model is markedly transversely isotropic, the velocity perpendicular to the plane of the layers being much lower than that parallel to it. With increasing stress, the velocity perpendicular to the plane of the layers increases rapidly until, at the highest stresses, it nearly equals that for the parallel direction, i.e. the model is very nearly isotropic.

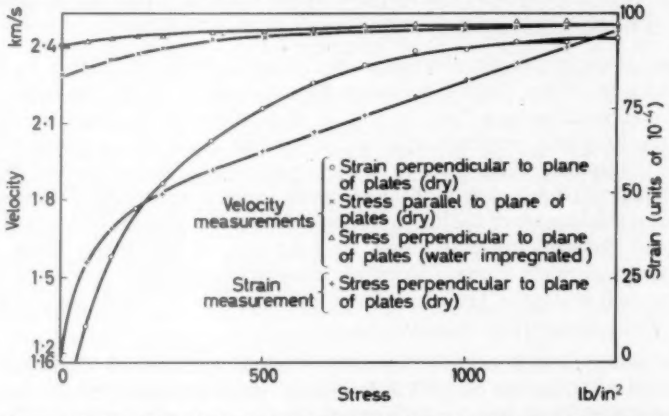

Figure 10. Variation of elastic wave velocity and strain with stress for a stack of 32 ebonite plates ($\frac{1}{8}$ in. thick)

It can be seen, comparing *Figure 3* with *Figures 9* and *10*, that the two models described above behave experimentally in a manner very similar to that observed for Barnsley Hards coal, i.e. the degree of anisotropy shows a similar dependence on stress; moreover the wave velocity increases with stress over the range of stress corresponding to the linear portion of the stress/strain curve. The effects of cleat cracks and random flaws, observed for the other coals tested, are not of course allowed for in the models.

For the final experiment, the plates were stacked under water; this provided a simple model for water-impregnated coal. The velocity/stress curve obtained for stresses perpendicular to the plane of the layers is shown in *Figure 10*. It is apparent that the effects obtained by water impregnation of the plates were similar to those obtained by water impregnation of Barnsley Hards coal, i.e. the wave velocity at zero stress was considerably increased and the subsequent increase of velocity with stress reduced (compare *Figures 7* and *10*).

A very rough estimate of the crack thicknesses between the ebonite plates may be made; the strain intercept (see *Figure 10*) is approximately $4{\cdot}6 \times 10^{-3}$. Thus, for a 4 in. cube, the total compression due to the closing of the cracks is $4{\cdot}7 \times 10^{-2}$ cm. As there are two steel–ebonite and 31 ebonite–ebonite interfaces, the mean crack thickness is of the order of 10 microns. An estimate of this sort is not possible for the coal samples without making a microscopic examination since although the total compression is of the same order (say for Barnsley Hards compressed perpendicular to the bedding plane—see *Figure 3*), the number of effective interfaces is not known. In view of the similarities between experimental behaviour of the model and the coal, it is likely that cavities in the model and the coal have comparable dimensions.

MICROSCOPIC OBSERVATIONS OF CRACKS IN BARNSLEY HARDS COAL

If, as has been suggested above, the anisotropic behaviour of coal is due to flat cavities a few microns thick, situated with their flat surfaces parallel to the bedding planes, a microscopic examination of the surface of a specimen of coal should show the ends of some of the cavities as line cracks oriented parallel to the bedding planes.

Some microscopic examinations were undertaken for the author by Price and Ashwin of the Mining Research Establishment. Three specimens were examined, each being a 2 in. $\times$ $\frac{3}{4}$ in. $\times$ $\frac{3}{4}$ in. prism of Barnsley Hards, cut with the long axis perpendicular to the bedding plane. Each specimen was highly polished and, using a high powered petrological microscope to observe light reflected from a surface of the specimen, a count was made of the number and total thicknesses of the line cracks, oriented parallel to the bedding planes, observed during a traverse along the long axis of the prism. Three such traverses were made for each specimen, the specimen being displaced laterally before each traverse. The microscope was capable of resolving cracks of thicknesses greater than about 0·5 micron.

The results shown in *Table 6* indicate that the mean crack width per unit length of coal is in the range 2 to 9 microns per millimetre. The mean strain intercept previously obtained[2] from the results of stressing ten 1·5 in. cubes of Barnsley Hards in a direction perpendicular to the bedding planes was

Table 6. Thickness of cracks in Barnsley Hards coal

Specimen	Length of traverse cm	Widths of cracks observed microns												Total number of cracks observed	Total crack thickness microns	Mean crack thickness microns	Mean crack width per unit length of coal microns/mm
1	2·47	2	8	1	80	2	8	2	2	4	4	8	4	12	125	10	5
	2·45	28	4	2	4	4	20	4	8	1	8	4	60	12	147	12	6
	2·46	8	4	8	40	80	40	16	2	4	4	4	20	12	230	19	9
2	2·88	8	16	60	8	20	8	16	4	—	—	—	—	8	140	18	5
	2·88	20	8	1	12	1	12	2	28	6	12	—	—	10	102	10	4
	2·87	6	8	8	60	20	4	20	—	—	—	—	—	7	126	18	4
3	3·11	12	8	4	8	8	8	8	8	—	—	—	—	8	64	8	2
	3·11	12	8	8	4	4	8	8	6	4	16	8	—	11	86	8	3
	3·13	2	8	24	6	4	4	8	4	8	6	10	—	11	84	8	3

$1{\cdot}6 \times 10^{-3}$; assuming that the strain intercept is due to the closing of cracks, this would suggest a mean crack width per unit length of coal of 1·6 micron per millimetre. The agreement between the two sets of results, obtained by quite different techniques, is remarkably close. It is not surprising that the microscopic examination gives the higher result, since here the total crack thicknesses are measured, whereas it is probable that in fact the strain intercepts measure only the partial closing of the cracks.

Some microscopic observations were made of the closing of cracks under stress. Several polished prisms of Barnsley Hards were used; each specimen was placed in a clamping frame so that stresses could be applied along the axis of the specimen, i.e. in the direction perpendicular to the bedding plane. Stresses were applied by tightening the bolts of the frame and the loads were measured by means of a calibrated load cell placed between the end of the specimen and the frame.

Figure 11(a), for example, shows a photomicrograph of cracks observed at zero stress in a vitrain band. *Figure 11*(b) shows the same cracks at a stress of 1 000 lb/in²; it can be seen that one of the cracks has almost completely closed under stress. The other crack shown appears to have hardly closed at all, possibly because of the inclusion of material during the polishing process. The crack size may be estimated from the scale shown; for all the photographs each small division was 4 microns. *Figure 12*(a) (zero stress) and *Figure 12*(b) (stress 1 500 lb/in²) show an example of a crack which partially closes under stress. All the cracks examined were observed to return to their original shapes when the stresses were removed. For all the photographs, care was taken to arrange correct focusing, since by a slight de-focusing, a crack can be made to appear to have closed. A scrutiny of the photographs shows that the cracks observed are oriented roughly parallel to the bedding plane. *Figure 13* (zero stress) shows the typical woodlike cell structure observed in the fusinite bands. It is very probable that structures of this type behave elastically when stressed, but deform more easily than the more homogeneous constituents of the coal. The deformation of such cavities, together with the further deformation of the cavities remaining after the partial closing of the larger cracks [see *Figure 12*(b)], probably accounts for the increase of elastic wave velocity with stress observed for the range of stresses corresponding to the linear portion of the stress/strain curves.

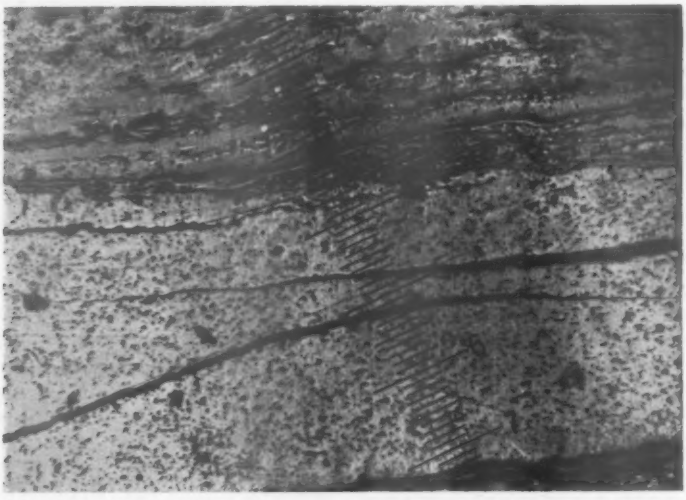

Figure 11(a). *Microcracks in clarain band of Barnsley Hards at zero stress (1 small division of scale = 4 microns)*

The results of *Table 6* show that the mean crack thickness, for the cracks observed, is in the range 8 to 19 microns, i.e. of the same order as that estimated for the stack of ebonite plates (10 microns), it seems likely, therefore, that the variation of velocity with stress observed for the model and the coal were similar because the cavities responsible were of similar dimensions and distributions.

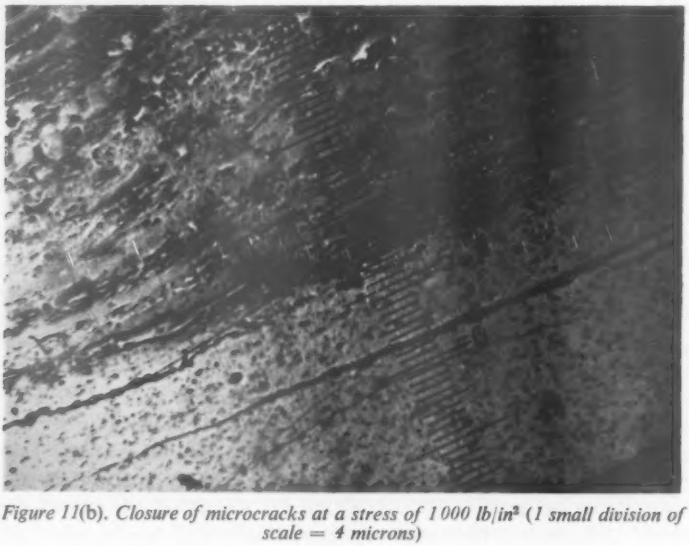

Figure 11(b). *Closure of microcracks at a stress of 1 000 lb/in² (1 small division of scale = 4 microns)*

DISCUSSION AND CONCLUSIONS

The measurements on Barnsley Hards, Pumpquart anthracite, Cwmtillery and Pleasley coal samples have shown that the elastic wave velocities perpendicular to the bedding planes, and for the heavily cleated coals, perpendicular to the cleat planes as well, are markedly dependent upon stress. The increase of elastic wave velocity as stress is applied in the direction perpendicular to the cleats is clearly due to the closing of the cleat cracks; the sometimes even

Figure 12(a). *Microcracks in clarain band of Barnsley Hards at zero stress (1 small division of scale = 4 microns)*

more pronounced increase of elastic wave velocity as stress is applied in the direction perpendicular to the bedding plane can be explained by the closing of a system of flat cracks, called here the 'layer cavities', which are oriented with their flat surfaces parallel to the bedding planes.

This conclusion is supported by the results of experiments involving the impregnation of Barnsley Hards coal with water and with phenyl salicylate. It has been shown that the elastic wave velocity perpendicular to the bedding plane (measured at zero stress) is considerably increased by impregnation, and the stress dependence of the wave velocity reduced. This is exactly the result which would be expected from the layer cavity hypothesis as a consequence of replacing the air in the cavities by a medium having a higher elastic wave velocity.

Figure 12(b). *Partial closure of microcracks at a stress of 1 500 lb/in² (1 small division of scale = 4 microns)*

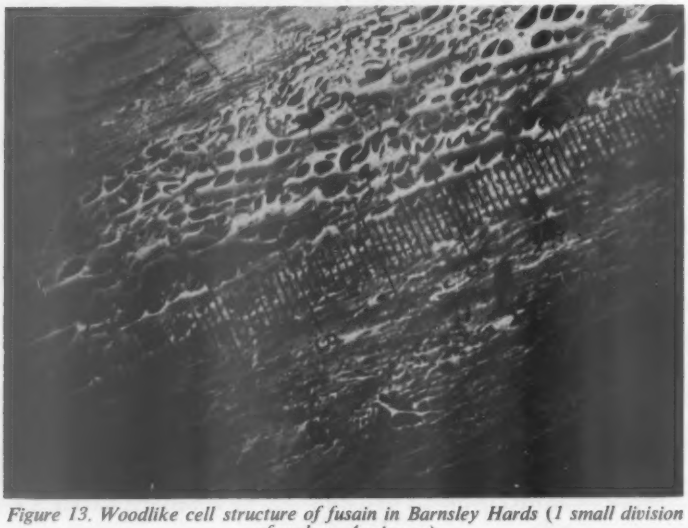

Figure 13. Woodlike cell structure of fusain in Barnsley Hards (1 small division of scale = 4 microns)

Experiments have shown that a model consisting of a pile of thin plates exhibits very similar characteristics, from the viewpoint of these measurements, to Barnsley Hards coal. That is, the pile and the coal are both transversely isotropic, at zero stress, with respect to the elastic wave velocity and the anisotropy depends on the external stress in a very similar manner, i.e. if high stresses are applied perpendicular to the plane of the layers, both the pile and the coal exhibit an isotropic symmetry. Moreover, the effects of water impregnation of the pile of plates (considering the elastic wave velocity perpendicular to the bedding plane) were similar to the effects of water impregnation of Barnsley Hards coal. The experimental results for the pile of plates are explained by the presence of microscopic cavities (mean thickness estimated at 10 microns) between neighbouring plates; since the model has been shown to be a reliable one, it is reasonable to assume that cavities of similar orientations are present in the coal samples.

The description given here of the layer cavities as disc-like cracks oriented with their flat surfaces parallel to the bedding plane of the coal may be an oversimplification. If, for example, there were present in the coal networks of tube-like capillaries with the tubes randomly oriented in directions parallel to the bedding planes, then the coal would exhibit transverse isotropy and the elastic wave velocity perpendicular to the bedding plane would decrease as stress was applied. The stress/strain curve, however, would be linear from the origin, assuming a linear elastic deformation of the tubes. Moreover, bearing in mind the formation of coal as a layered material, subjected to high stresses for long periods of time, it seems very possible that, as these stresses are relieved in the mining processes, parting cracks occur between the layers of the more weakly bonded macerals. Cavities in this way would in fact correspond more to the flat disc type of crack than to the capillary tube network.

A microscopic examination of Barnsley Hards specimens has disclosed cracks, of thicknesses of the order of 10 microns, oriented parallel to the bedding plane. Some of these were observed to close, or partially close, under stress. The mean crack width per unit length of coal was found to lie in the range 2 to 9 microns per millimetre and is of the same order as that estimated from the stress/strain curves. *Figure 1* shows the orientation of the microcrack structure (for cracks of micron sizes) suggested for a coal such as Barnsley Hards, where the cleating is confined, for small specimens, to the relatively thin vitrain bands. It is almost self-evident from the figure that such a structure would be responsible for an anisotropy in the elastic wave velocities; only in the direction parallel to the bedding plane are there likely to be paths for the elastic waves which do not involve a crossing of the layer cavities.

The work has illustrated one of the fundamental differences in the dynamic and static methods of measuring the elastic moduli of coal. The static measurements are made when the coal has a 'closed' or partially closed microcrack structure, in contrast to the 'open' structure measured in the usual way by dynamic techniques.

Although this work has shown that the elastic anisotropy is mainly due to an anisotropic microcrack structure, it is probably that the coal would always exhibit some transverse isotropy because of differences in the elastic moduli

of the layers and also, for coals of high carbon content, because of the low crystallinity of the coal substance. It would be interesting to repeat the measurements of Schuyer, Dijkstra and van Krevelen[4] on thin samples of vitrain, but with an arrangement to vary the external stresses on the samples; this would determine whether the anisotropy they observed for the high carbon coals was due to the microcrack structure or, as they have suggested, to an anisotropy in the bonding forces between particles in the basic coal substance.

Some support for the layer cavity hypothesis is obtained from a consideration of the anisotropy of the crushing strengths of the coals measured. It is probable that the breakage of cubes of coal under uniaxial compression is due to tensile failure in a direction perpendicular to the direction of compression. Thus it might be expected that the existence of cracks (layer cavities) parallel to the bedding plane would facilitate comparatively easy tensile breakage perpendicular to the bedding planes when the crushing stresses were applied parallel to the bedding planes. That this is in fact so is apparent from the work of C. D. POMEROY[9], who has made uniaxial compressive tests on many different British coals including those examined in the present work.

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The Chlorination of Low Rank Coals with (a) *Sulphuryl Chloride, and* (b) *Hydrogen Peroxide–Hydrochloric Acid*

F. J. PINCHIN

Two coals of low rank have been chlorinated with sulphuryl chloride. Both side-chain and nuclear substitution occur in the absence of added catalysts. In the presence of an ionic-type catalyst (aluminium chloride) or peroxide-type catalysts (benzoyl or di-t-butyl peroxides) there is further substitution, most probably in the aromatic nuclei of the coal molecules. The organic peroxide catalysts do not appear to cause specific side-chain substitution when using sulphuryl chloride with these coals. Hydrogen peroxide–hydrochloric acid, which generates free chlorine (probably as chlorine atoms) is less effective as a chlorinating agent; but even with this both types of chlorination occur. In all cases the lower rank coal took up the least chlorine. These results suggest that when specific chemical reagents are used with coals, caution should be observed in interpreting results. In the present case the failure of the organic peroxides to direct the chlorine into the side chains appears to be due to the fact that extensive side-chain chlorination occurs in the absence of an added catalyst. The ash or peroxides present in the coals themselves may, however, influence apparently uncatalysed reactions.

COALS probably contain aromatic, alicyclic and aliphatic groups; it may thus be possible by the use of specific reagents to attack particular parts of the coal molecules. This paper considers chlorination from such a viewpoint.

Sulphuryl chloride in the presence of benzoyl peroxide is said to produce atomic chlorine, which reacts with organic compounds such as toluene to give side-chain chlorination[1, 2]. I. G. C. DRYDEN[3] has chlorinated ethylene diamine coal extracts using this reagent in chloroform suspension and solution.

Sulphuryl chloride reacts with anthracene[4] and acenaphthene[5] in the absence of a catalyst; with most aromatic compounds in the presence of aluminium chloride it gives nuclear substitution[2, 6]; and it gives side-chain peroxide catalysed chlorination with compounds such as toluene[1, 2]. The reactions of two coals with sulphuryl chloride have now been investigated:

(*i*) in the absence of an added catalyst, and
(*ii*) with benzoyl peroxide or di-*t*-butyl peroxide (DTBP), or
(*iii*) aluminium chloride, as added catalysts.

Hydrogen peroxide–hydrochloric acid mixtures have been used for the nuclear chlorination of anisole and 2-methoxynaphthalene[7], while hydrogen peroxide–hydrochloric acid in the presence of acetic acid and nitrobenzene caused chlorination of perylene in the 3 : 9 positions[8]. The use of these reagents with coals has been investigated briefly, since they also involve the formation of free chlorine (probably as chlorine atoms).

CHLORINATIONS WITH SULPHURYL CHLORIDE

In the preliminary experiments (CD3 and CD0) the coal (dried in air at 105°C) was suspended in carbon tetrachloride; benzoyl peroxide (100 per cent) and sulphuryl chloride (99 per cent; 6 ml) were added. After 1 hour at reflux another 4·5 ml sulphuryl chloride was added and refluxing continued for a further hour (*Table 1*). Evolved gases were absorbed in 10 per cent

Table 1. Chlorination of coals with sulphuryl chloride

Expt No.	Coal	Dry wt g	Time min	CCl_4 ml	SO_2Cl_2 ml	Catalyst		Dry product g	Cl content % (dry basis)	
						Nature	g		On wt gain	By analysis
CD3	*D III*	5·20	115	50	10·5	*Benz. per.*	0·06	6·75	23·0	17·7
CD0	*D0*	4·18	115	50	10·5	*Benz. per.*	0·06	4·95	15·6	11·7
BSCC/1	*D III*	15·02	95	100	10·5	*Benz. per.*	0·36	19·66	23·6	19·7
BSCC/2	*D0*	16·69	95	100	10·5	*Benz. per.*	0·37	19·33	13·7	11·3
PSCC/1	*D III*	15·70	120	100	10·5	*DTBP*	0·5ml	19·63	20·0	17·2
PSCC/2	*D0*	16·29	120	100	10·5	*DTBP*	0·5ml	18·29	10·9	9·3
ASCC/1	*D III*	15·98	120	100	10·5	$AlCl_3$	0·565	20·60	22·5	20·2
ASCC/2	*D0*	16·69	120	100	10·5	$AlCl_3$	0·695	18·60	10·1	10·2
SCC/1	*D III*	16·14	90	100	10·5	*None*	*None*	20·38	20·8	15·7
SCC/2	*D0*	15·96	90	100	10·5	*None*	*None*	17·94	11·1	9·7

NOTE: The percentage weight gain can be used as a rough estimate of the amount of chlorination; this is useful in planning subsequent experiments.

sodium hydroxide. The product was filtered and dried in air at 105°C. From the filtrates, 0·05 to 0·07 g (per experiment) of a brown solid was recovered but since this amounted to only 1 to 2 per cent w/w of the coal it was not further examined.

The reaction appeared to be complete within a quarter of an hour of adding the sulphuryl chloride. In subsequent experiments therefore, the excess of sulphuryl chloride was reduced, and a slightly different technique adopted, the experiments being carried out in nitrogen to minimize oxidation (and possible inhibition).

The coal (vacuum dried at 100°C) was weighed into a flask containing the catalyst. Carbon tetrachloride and sulphuryl chloride were added and the mixture brought to reflux with occasional shaking (water bath temperature about 88°C). The product was treated as before, and dried *in vacuo* for about 16 hours (*Table 1*).

CHLORINATIONS WITH HYDROGEN PEROXIDE–HYDROCHLORIC ACID

A preliminary experiment (HPCL/1) used the method of L. JURD[7]. The coal was suspended in aqueous hydrochloric acid and 30 per cent hydrogen peroxide added over 40 min; after a further 20 min the product was filtered, washed and dried in air at 105°C. Since the chlorine content was only 3·9 per cent (dry basis), the method of A. ZINKE *et al.*[8], described below, was investigated.

The coal was suspended in concentrated hydrochloric acid and glacial acetic acid, brough to reflux and a mixture of 30 per cent hydrogen peroxide

and glacial acetic acid added gradually. The reaction was vigorous. After further reflux, the filtered, washed product was dried first in air at 100°C and then *in vacuo* at 100°C to ensure removal of hydrogen chloride (*Table 1*).

RESULTS

The coals used were from the 9 ft seam, Binley, Warwick (D0); and an Ellington High Main, Northumberland (DIII). They were both of low rank (VM 34·5 and 32·4 per cent respectively) and were ground to pass a 72 B.S. sieve.

Table 2. Chlorination of coals with hydrochloric acid–hydrogen peroxide

Expt No.	Coal	Dry wt g	Time min	Solvent		Added reagent		Dry product g	Cl content % (dry basis)	
				Nature	ml	Nature	ml		On wt gain	By analysis
HPCL/1	D III	9·44	60	Water Conc. HCl	40 40	H_2O_2	40	9·82	3·9	3·9
HPCL/2	D III	10·00	30	Conc. HCl Acetic	30 50	H_2O_2 Acetic	30 30	11·40	12·2	9·7
HPCL/3	D III	26·67	45	Conc. HCl Acetic	100 150	H_2O_2 Acetic	90 90	30·87	13·6	12·7
HPCL/4	D0	26·60	45	Conc. HCl Acetic	100 150	H_2O_2 Acetic	90 90	27·29	2·5	8·4

NOTE: 10 to 20 ml water was added to wash in the coal in Run HPCL/2.

Details of the experiments are given in *Tables 1* and *2*, and analyses of the coals and products in *Table 3*. The products were black and coal-like. The code numbers SCC, BSCC, PSCC and ASCC refer to the non-catalysed reactions and to those catalysed with benzoyl peroxide, di-*t*-butyl peroxide and aluminium chloride, respectively.

Table 3. Analyses of coals and chlorinated coals (dry ash-free basis %)

Coal or product	C	H	N	S	O + errors	Cl
D III coal (used for Run CD 3)*	81·6	5·1	0·9	1·2	11·2	*n.d.*
CD 3 product	61·5	3·6	1·3	1·7	13·9	18·0
D0 coal (used for Run CD0)*	76·8	5·3	1·4	1·7	14·8	*n.d.*
CD0 product	61·0	4·1	1·0	2·7	19·1	12·1
*D III coal**	80·95	5·1	1·8	1·5	10·6	0·05
*D 0 coal**	76·6	4·9	1·1	2·7	14·6	0·1
Products						
BSCC/1 (D III)	63·1	3·3	1·3	2·0	10·2	20·1
PSCC/1 (D III)	66·1	3·5	1·5	2·0	9·2	17·7
ASCC/1 (D III)	63·0	3·4	1·4	1·8	9·7	20·7
SCC/1 (D III)	63·9	3·5	1·4	2·1	13·0	16·1
BSCC/2 (D0)	67·1	3·9	1·0	2·8	13·0	12·2
PSCC/2 (D0)	69·2	4·1	1·1	2·8	12·6	10·2
ASCC/2 (D0)	68·2	3·8	1·1	2·9	12·8	11·2
SCC/2 (D0)	69·8	3·8	0·9	3·1	11·7	10·7
HPCL/3 (D III)	68·0	3·6	1·3	1·2	13·0	12·9
HPCL/4 (D0)	68·8	3·8	0·9	2·2	15·5	8·8

* The D III and D0 coals used in the preliminary experiments were different samples from those used in the remainder of the work.

EXAMINATION OF PRODUCTS

(a) *Hydrolysis with aqueous sodium hydroxide*

The chlorination products (2 to 4 g) were refluxed for 4 h with 100 ml 10 per cent sodium hydroxide. This should remove aliphatic and alicyclic substituted chlorine by hydrolysis; it is likely that little, if any, aromatic chlorine would be removed under these mild conditions. No precautions were taken to minimize oxidation in these experiments. Humic material interfered with titration of the filtrate for chloride ion (Mohr's method), and the humic material consumed some silver nitrate so that these results (particularly with the D0 coal) are probably a little high (*Table 5*).

Table 4. Composition of coals and chlorinated coals
g atoms/100 g atoms carbon

Run No.	*g atoms/100 g atoms carbon*						Δ H(−)	Δ O(+)
	C	H	N	S	O	Cl		
DIII coal (used for Run CD3)	100	75·3	1·0	0·6	10·2	—	—	—
DIII coal	100	74·7	2·0	0·7	9·8	—	—	—
D0 coal (used for Run CD0)	100	82·2	1·5	0·9	14·5	—	—	—
D0 coal	100	75·9	1·4	1·4	14·1	—	—	—
CD3	100	69·5	1·9	1·1	16·8	9·9	5·8	5·6
BSCC/1	100	63·8	1·8	0·9	9·5	10·8	10·9	0·3
PSCC/1	100	64·2	2·1	1·1	10·6	9·0	10·5	0·8
ASCC/1	100	65·3	2·0	1·0	11·9	11·1	9·4	2·1
SCC/1	100	65·3	2·0	1·2	15·2	8·5	9·4	5·4
CD0	100	81·1	1·5	1·7	23·5	6·7	1·1	9·0
BSCC/2	100	70·3	1·2	1·5	14·4	6·2	5·6	0·3
PSCC/2	100	71·5	1·3	1·5	13·6	5·0	4·4	(−0·5)
ASCC/2	100	67·4	1·4	1·6	14·0	5·6	12·5	(−0·1)
SCC/2	100	64·5	1·3	1·6	12·5	5·3	11·4	(−1·6)
HPCL/3	100	65·1	1·7	0·7	14·2	6·5	9·6	4·4
HPCL/4	100	65·9	1·1	1·2	16·9	4·3	10·0	2·8

Table 5. Removal of chlorine from products

Run No.	Cl *removed % of Total*		Cl *g atoms/100 g atoms carbon*				
	by KOAc	*by* NaOH	*Present*	*Removed by* KOAc	*Left by* KOAc	*Removed by* NaOH	*Left by* NaOH
SCC/1	55	80	8·5	4·7	3·8	6·8	1·7
PSCC/1	46	—	9·0	4·1	4·9	—	—
BSCC/1	46	66	10·8	5·0	5·8	7·1	3·7
ASCC/1	42	—	11·1	4·7	6·4	—	—
CD3	—	73	9·9	—	—	7·2	2·7
SCC/2	69	94	5·3	3·7	1·6	5·0	0·3
PSCC/2	67	—	5·0	3·4	1·6	—	—
BSCC/2	59	86	6·2	3·7	1·5	5·3	0·9
ASCC/2	64	—	5·6	3·6	2·0	—	—
CD0	—	88	6·7	—	—	5·9	0·8
HPCL/3	50	—	6·5	3·3	3·2	—	—
HPCL/4	64	—	4·3	2·7	1·6	—	—

(b) *Treatment with potassium acetate*
Potassium acetate–glacial acetic acid removes chlorine from aliphatic groups either by esterification or by removal of hydrogen chloride[9]. The chlorinated products (5 g) were refluxed under nitrogen with 5 g freshly fused potassium acetate and 50 ml glacial acetic acid.

Titration of the washings with silver nitrate gave the percentage of chlorine removed (*Table 5*).

(c) *Effect of heating to 1000°C*
A. ECCLES, G. H. KENYON and A. MCCULLOCH[10] reported that the chlorine from their chlorinated coals was removed quantitatively as hydrogen chloride on heating to 600°C; E. BEYERS and D. VAN ROOGEN[11] reported that with their products, chlorine was also evolved above 600°C. The amounts of chlorine removed from the present product as hydrogen chloride on heating to 1000°C are given below (as percentage of total chlorine present). No free chlorine was evolved.

BSCC/1	86 per cent	BSCC/2	60 per cent
SCC/1	100 per cent	SCC/2	71 per cent
HPCL/3	80 per cent	HPCL/4	76 per cent

Since this was unpromising as a method of analysis for total chlorine further determinations were not carried out.

(d) *Infra-red spectra*
The i.r. spectrum of the chlorinated DIII coal (CD3) was examined by J. K. BROWN. There was a marked reduction in the methylene absorption consistent with chlorination of side chains or of non-aromatic material. Changes in the weak aromatic C—H absorption could not be detected because of interference by absorbed carbon tetrachloride. The hydrolysed material did not show much increase in the C—O absorption characteristic of aliphatic or alicyclic alcohols, but changes observed were consistent with the presence of salts of carboxylic acids (confirmed by the increase in ash content).

DISCUSSION

Chlorinations with sulphuryl chloride–benzoyl peroxide and with hydrogen peroxide–hydrogen chloride probably both proceed via free chlorine, either as atoms or molecules. The presence of free chlorine was observed (smell) in experiments HPCL/3–4, and with concentrated hydrochloric acid is reported in the literature (although there is a limiting concentration of both reactants below which free chlorine is not formed[12]). With sulphuryl chloride, it has been stated[13] that the reversible molecular dissociation of sulphuryl chloride to chlorine and sulphur dioxide is so rapid that it is unnecessary to postulate the existence of the $\cdot SO_2Cl$ radical. If this is so then probably both in the ionic-catalysed and non-catalysed reactions, some free chlorine is always present as atoms or molecules. The exact details of the radical mechanism are still unsettled[14].

Table 4 shows the changes in g atoms/100 g atoms of carbon on chlorination; this assumes no loss in carbon, which is substantially true.

Clearly substitution predominates with a DIII coal (Cl added = H removed) while with a D0 coal substitution occurs in the presence of a peroxide catalyst; dehydrogenation also occurs with aluminium chloride or in the absence of a catalyst (experiments CD3 and CD0, where much oxidation occurred, are disregarded here). Oxidation was suppressed where precautions were taken with D0 coals, but with DIII coals some oxidation did occur.

From *Table 3* it appears that benzoyl peroxide or aluminium chloride give very similar results, and give more chlorine uptake than with di-*t*-butyl peroxide, or with no added catalyst. Also it appears that a DIII coal takes up more chlorine than a D0 coal.

By sodium hydroxide hydrolysis or potassium acetate treatment, much chlorine is removed from the products (*Table 5*). Potassium acetate should remove aliphatic or alicyclic (side-chain) chlorine[9]; sodium hydroxide might remove some nuclear chlorine. In *Table 5* the changes (in g atoms/100 atoms of carbon) in the number of chlorine atoms present, are given. *Table 5* shows that, with products made using sulphuryl chloride as chlorinating agent, the number of chlorine g atoms/100 g atoms of carbon which can be removed from a given product by treatment with potassium acetate is approximately the same whether a catalyst was used in the chlorination or not. With sodium hydroxide similar remarks apply, although the amounts are different. These results imply that the catalyst does not direct extra chlorine into the side chains; it is more likely that both with aluminium chloride and with peroxide catalysts, most of the extra chlorine goes into the aromatic nuclei of the coal molecules. There is thus no evidence that peroxides cause specific side-chain chlorination in this particular case.

It is worth noting that the coals contain iron compounds in the mineral matter sufficient to form about 1 to 2 per cent of ferric chloride; this quantity would be sufficient to catalyse ionic chlorination reactions. Peroxide groups are present in the coal molecules (for a sample of DIII coal a peroxygen content of 28×10^{-5} g per g of coal has been quoted[15]). Hence the coals themselves contain materials which could catalyse chlorinations, so that even in the absence of added catalysts the reactions may not be uncatalysed.

In this particular reaction the added catalysts have little effect because the 'uncatalysed' reaction is so extensive, and hence their specific directive influences cannot be exercised readily. It is well to bear in mind that where only nuclear or only side-chain sites are available the chlorine may go into these positions regardless of the influence of the catalyst itself.

The results of chlorination with sulphuryl chloride, bromination in chloroform (J. K. BROWN *et al.*[16]), and chlorination in aqueous suspension (F. J. PINCHIN[17]) are compared in *Table 6*. Here the selected chlorination conditions gave primarily aliphatic substitution and the bromination mainly aromatic substitution; but the method of assessment (hydrolysis with 10 per cent sodium hydroxide) is far from being a precise one. The chlorine could account for 9 per cent (D0) and 20 per cent (DIII) of the aliphatic hydrogen estimated to be present (see ref. 16, Table 6); if all the aliphatic hydrogen were assumed to be in methylene groups, and if one hydrogen atom per methylene group

were available for substitution, then the chlorine could account for 18 per cent (D0) and 40 per cent (DIII) of the available aliphatic sites. Bromination could account completely for all of the aromatic hydrogen available in these coals.

Table 6. Comparison of chlorination and bromination of coals

Analysis g atoms added per 100 g atoms of carbon

Coal %C d.a.f.	*D0* 76·6%		*DIII* 81·0%		*DVI* 83·5%
Element	*Chlorination (a)*	*Bromination (b)*	*Chlorination (a)*	*Bromination (b)*	*Chlorination (c)*
H	−5·6	−16·5	−11	−14	−18
Br	—	11	—	12	—
Cl	6·2	—	11	—	13
O	0	4	0	1	7
% halogen removed by NaOH	88	30 *to* 40	73	30 *to* 40	60

NOTE: Conditions were: (*a*) SO_2Cl_2 in CCl_4 with benzoyl peroxide as catalyst at reflux (2 h). (*b*) Br_2 in $CHCl_3$ at 0°C (24 h). (*c*) Cl_2 in aqueous suspension at 0° to 10°C (2 h).

CONCLUSIONS

It is clear that the DIII coal takes up more chlorine than the D0 coal, whatever the reaction conditions. The presence of an added catalyst does not have a marked effect on the sulphuryl chloride reactions, although the chlorine uptake is increased by a significant amount. Side-chain and some nuclear substitution occur in the absence of an added catalyst, and in the presence of a catalyst further chlorination appears to be in the aromatic nuclei. The peroxide-type catalysts do not appear to cause specific side-chain chlorination with sulphuryl chloride. Hydrogen peroxide–hydrochloric acid is less effective as chlorinating agent, but even here both side-chain and nuclear chlorination appear to occur.

These results suggest that when specific chemical reagents are used with coals caution is necessary in interpreting the results.

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The Variability of Vitrinites in British Coal Seams

L. H. LEIGHTON

The variability in selected properties of a number of vitrinites in a range of British coals has been studied with particular reference to the coals of Yorkshire. The variability of Yorkshire vitrinites of a given rank level is found to approach that of the normal clarains on which the Seyler coal band is based. This finding is discussed in relation to the conclusion of van Krevelen that from petrographic examinations of coal and reflectance measurements on vitrinite the whole ultimate composition of a coal can be calculated.

IT IS now common knowledge that the properties of coal are determined by two main parameters: rank and petrographic composition. Rank may be expressed in different ways for differing purposes, but a common mode of expression is in terms of carbon content. Petrographic composition is generally taken to mean composition in terms of the maceral groups* vitrinite, exinite and inertinite. Each of these maceral groups comprises a number of macerals which are similar (though not identical) in appearance under the microscope.

While the dependence of chemical properties of coal on rank has been studied and documented for decades, it is only recently that the techniques of quantitative petrographic analysis have advanced sufficiently to enable coal scientists to achieve marked progress in their efforts to quantify the dependence of these properties on petrographic composition. Within the last few years three independent groups of continental workers[1–3] have published the results of extended researches into the properties of maceral groups at various levels of rank. A parallel study of British coals is currently in progress in the Yorkshire laboratories of the Coal Survey branch of the Scientific Department of the National Coal Board.

These researches all have a common general pattern. The coal samples were subjected to crushing and selective flotation so as to yield concentrates of one or more of the maceral groups, the properties of the concentrates were determined, and attempts were made to correct for petrographic impurity the determinations relating to each group. These operations produced series of results enabling the properties of the maceral groups in coals of a range of rank to be compared and contrasted.

None of the studies mentioned was primarily concerned with the variability to be found within a maceral group at a particular level of rank. It was, of course, realized that the members of a group are not identical in their properties, but it was rightly felt that the differences between these members are

* The petrological terms used herein are those promulgated by the Nomenclature Subcommittee of the International Committee of Coal Petrology in their *Glossary of Coal Petrology* (1957).

much smaller than those between different groups and could therefore be ignored as a first approximation.

The present work is an account of investigations into the variability found in some of the chemical properties of the vitrinite group in the range of rank covered by the coals of the Yorkshire Coalfield (about 82 to 87 per cent carbon). Vitrinite-rich material from a few coals of higher rank have also been examined and are included for purposes of comparison.

EXAMINATION OF VITRINITES

Vitrinites in Yorkshire coal seams

Two investigations were conducted: one into the variability of vitrinite in different vitrain bands in the same coal sample, and the other into the differences between vitrinite in vitrain bands and that in vitrainous clarain from the same lump. It had been hoped that it would be possible to prepare a sample of vitrinite of absolute purity from each selected source, but preliminary experiments demonstrated this to be impracticable. The work was therefore carried out on carefully selected vitrains and clarains of high vitrinite content (usually 95 per cent or more) and often with less than 1 per cent mineral matter.

Vitrinites in vitrain bands—Nine working faces in eight Yorkshire seams were visited and a set of vitrain bands was taken from each face. Each set comprised from 2 to 12 separate bands picked out from pillar samples or from different points in close juxtaposition on the face. Analytical samples were obtained by careful selection of material of obviously high purity from each band. They all contained 93 per cent or more of vitrinite.

Table 1 shows the analytical data obtained. The range of analysis was unavoidably limited, as in many cases the samples were extremely small, but it has been sufficient to demonstrate the order of variability that exists. The range of carbon content (dry ash-free) within a set was usually not more than 0·4 per cent (occasionally 0·6 per cent), hydrogen contents were generally constant within experimental error, and volatile matter (dry ash-free) showed a range of up to 2·8 per cent. In some of the sets part of the variation found may possibly be attributed to the small petrographic differences between the constituent vitrains, but in others (for example, those from the Top Haigh Moor seam at West Riding Colliery and samples 6192 and 6196 from the Warren House seam at Prince of Wales Colliery) it seems clear that the vitrinites themselves showed significant differences of the order quoted.

A Gieseler plastometer became available for the examination of the later sets of vitrains and an interesting phenomenon was observed; the pairs of vitrains from the Winter seam at Wharncliffe Woodmoor 1, 2, 3 Colliery showed very similar 'fluidities', as did those from the Thorncliffe seam at Woolley Colliery, but those from the Top Haigh Moor seam at West Riding and the Fenton seam from Wharncliffe Woodmoor 1, 2, 3 showed marked differences. The West Riding samples (6929 to 6931) were all virtually pure vitrinites and sample 6930 behaved very differently from the other two—it attained a measurable fluidity and left a residue of fused coke, whereas the other two had practically no fluidity and left non-coherent powdery residues.

Table 1. Analysis of vitrain bands

Table 1. Analysis of vitrain bands

Seam and colliery	*Flockton Thick—Allerton Bywater*				*Top Haigh Moor—Wharncliffe Woodmoor 4 & 5*											*Warren House—Prince of Wales*					
Sample ref. No.	*5668*	*5669*	*5671*	*5672*	*6080*	*6085*	*6084*	*6086*	*6087*	*6089*	*6078*	*6079*	*6081*	*6082*	*6088*	*6083*	*6194*	*6191*	*6195*	*6192*	*6193*	*6196*
Chemical analysis																						
Dry basis																						
Ash	2·0	1·1	1·5	1·0	0·4	0·3	0·2	0·5	0·2	0·3	0·2	0·3	0·2	0·3	0·2	0·6	1·0	0·8	1·2	0·9	0·7	0·9
Dry ash-free basis																						
Carbon	83·0	82·7	82·4	82·9	86·3	86·3	86·1	86·1	86·2	86·3	86·2	86·1	85·9	86·0	86·3	86·0	83·6	83·5	83·4	83·8	83·6	83·2
Hydrogen	5·2	5·5	5·3	5·4	5·4	5·4	5·4	5·5	5·4	5·5	5·4	5·5	5·5	5·5	5·4	5·4	5·4	5·3	5·3	5·2	5·4	5·3
Volatile matter	35·9	37·6	38·5	37·1	33·7	33·5	33·9	34·2	33·8	34·3	33·7	34·2	34·2	34·4	34·0	33·0	35·9	36·2	35·4	34·9	35·5	34·6
Plasticity data (Gieseler)																						
Maximum fluidity (div/min)																						
Petrographic analysis																						
Maceral distribution																						
Vitrinite	97	97	95	94	96	96	97	97	97	97	97	97	97	97	97	99	97	97	98	98	98	98
Exinite	1	2	2	1	1	2	1	1	1	1	2	2	2	2	2	*Trace*	1	1	—	*Trace*	1	—
Inertinite	2	1	3	5	3	2	2	2	2	2	1	1	1	1	1	—	2	2	2	2	1	1

Seam and colliery	*Kents Thick—Sharlston*		*Middleton Little—Lofthouse*			*Winter—Wharncliffe Woodmoor 1, 2, 3*		*Top Haigh Moor—West Riding*			*Fenton—Wharncliffe Woodmoor 1, 2, 3*		*Thorncliffe—Woolley*	
Sample ref. No.	*5545*	*5546*	*5974*	*5975*	*5972*	*6948*	*6949*	*6929*	*6930*	*6931*	*6981*	*6984*	*7122*	*7123*
Chemical analysis														
Dry basis														
Ash	0·8	2·8	1·9	1·4	1·7	0·4	0·5	1·0	1·5	0·6	2·9	1·2	1·0	0·9
Dry ash-free basis														
Carbon	84·4	84·4	85·2	85·8	85·7	85·0	85·1	84·0	83·6	83·8	86·0	86·2	86·5	86·4
Hydrogen	5·3	5·4	5·6	5·5	5·4	5·2	5·2	5·2	5·3	5·3	5·5	5·5	5·4	5·3
Volatile matter	—	—	—	—	—	34·5	33·0	34·5	37·3	—	34·1	34·6	34·3	34·4
Plasticity data (Gieseler)														
Maximum fluidity (div/min)	—	—	—	—	—	50	30	10	150	6	11 000	5 300	7 500	5 200
Petrographic analysis														
Maceral distribution														
Vitrinite	98	97	93	94	98	94	99	100	100	100	98	97	93	94
Exinite	1	—	2	2	—	3	1	—	—	—	1	1	4	3
Inertinite	1	1	5	4	2	3	—	—	—	—	1	1	3	2

The vitrains from the Fenton seam at Wharncliffe Woodmoor were less pure in terms of vitrinite content but were petrographically identical, and although they were both very 'fluid' one was markedly more so than the other. These observations add support to the other analytical evidence that real differences can exist between vitrinites in one and the same coal.

Several of the samples were etched and there were indications that, although they were all telinitic (i.e. they showed signs of cell structure), the degree of preservation of cell structure varied between different samples. The very fact that one can observe structure in vitrinite by differences in reflectance between cell walls and fillings suggests the probability of corresponding differences in the composition of walls and fillings, and that in turn suggests that samples differing in the proportion of wall to filling will also differ in chemical properties. There may well be a continuous range of degree of preservation of cell structure in vitrinites, and it is therefore to be expected that variations in properties will exist.

Comparison of vitrinite in vitrain bands with vitrinite in clarain—For this investigation pairs of samples were obtained from eight sources. Each pair consisted of one or more vitrain bands and a sample of very bright clarain from the same source. Where more than one vitrain band was used, the bands were regarded as one sample and from them was prepared by careful selection one analytical sample of vitrinite of high petrographic purity.

It was not possible to prepare equally pure vitrinite from the clarains but here again careful selection produced samples with generally more than 93 per cent vitrinite.

The analyses are recorded in *Table 2*. The difference in carbon content between the two samples in each pair is of the same order as in the investigations above but in some cases both hydrogen and volatile matter show greater differences. Because of the petrographic heterogeneity of the clarains it is generally difficult to assess how much of this increased variability is a reflection of differences in the vitrinite component, but it is indisputable that in two cases (the Warren House at Askern and the Barnsley at Rossington) the differences are too great to be explained away on the basis of the maceral analyses alone.

The behaviour of the samples in the plastometer is again most interesting. The first six pairs of samples behaved in the same self-consistent manner: in each case the vitrain was much less 'fluid' than the clarain and the onset of softening occurred at a higher temperature than in the clarain. As in each case the clarain had also the higher volatile matter and a greater proportion of exinite, it is tempting to speculate that the differences are in some way related to the exinitic component. However, the samples from the Fenton seam at Wharncliffe Woodmoor did not conform to this pattern of behaviour. In the pair of samples 6981 and 6982 the vitrain was more 'fluid' than the clarain although the grouped maceral composition was the same (within experimental limits). Samples 7834 and 7835 were repeat samples taken to confirm this observation; these repeat samples differed significantly in composition from the earlier pair and showed the effect more markedly. That the effect noted should be repeated supports the belief that there are differences within the

Table 2. Comparison of vitrinite from vitrain bands and bright clarain

Seam	*Parkgate*		*Parkgate*		*Winter*		*Warren House*		*Barnsley*		*Barnsley*		*Fenton*		*Fenton*	
Colliery	*Aldwarke*	*Kilnhurst*	*Houghton Main*		*Wharncliffe Woodmoor 1, 2, 3*		*Askern*	*Skellow*	*Rossington 20*		*Yorkshire Main*		*Wharncliffe Woodmoor 1, 2, 3*		*Wharncliffe Woodmoor 1, 2, 3*	
Source of vitrinite	*Vitrain*	*Clarain*	*Vitrain*	*Clarain*	*Vitrain*	*Clarain*	*Vitrain*	*Clarain*	*Vitrain*	*Clarain*	*Vitrain*	*Clarain*	*Vitrain*	*Clarain*	*Vitrain*	*Clarain*
Sample ref. No.	*S14066*	*S14068*		*S12984*	*6948*	*6946*	*S15603*	*S15604*	*S15847*	*S15848*	*S10297*	*S10298*	*6981*	*6982*	*7834*	*7835*
Chemical analysis																
Dry basis																
Ash	1·1	1·5	—	1·3	0·4	0·9	1·6	1·3	2·1	2·5	0·9	1·6	2·9	1·9	3·3	3·8
Dry ash-free basis																
Carbon	86·9	86·7	—	86·4	85·0	84·8	83·0	82·7	82·5	82·8	85·7	84·6	86·0	86·3	85·0	85·5
Hydrogen	5·4	5·5	—	5·6	5·2	5·3	5·2	5·6	5·0	5·4	5·2	5·4	5·5	5·6	5·3	5·3
Volatile matter	33·0	35·9	—	34·8	34·5	35·3	35·5	41·9	33·7	39·8	33·3	36·7	34·1	34·1	35·6	34·4
Plasticity data (Gieseler)																
Temperature when fluidity exceeds 5 div/min °C	423	415	423	415	419	417	423	415	—	413	422	417	406	410	411	408
Temperature of maximum fluidity (°C)	461	•	455	•	440	444	439	441	425	432	445	448	449	446	448	444
Maximum fluidity (div/min)	1440	>20 000	670	>20 000	48	108	13	205	2	13	165	390	11 100	7 200	6 200	2 120
Petrographic analysis																
Maceral distribution																
Vitrinite	98	96	98	97	94	92	99	90	99	94	99	94	98	97	98	93
Exinite	*Trace*	2	1	2	3	6	*Trace*	5	—	3	—	3	1	2	1	6
Inertinite	2·0	2	*Trace*	1·0	3	2	1	5	1	3	1	3	1	1	1	1
Microlithotype distribution																
Vitrite	94	63	95	56	89	74	—	33	—	44	—	53	97	87	95	79
Clarite	2	31	4½	43	10	23	—	52	—	50	—	37	2	12	4	18
Claro-durite	3	5	—	1	1	2	—	3	—	5	—	9	—	*Trace*	1	2
Durite	—	—	—	—	—	1	—	—	—	*Trace*	—	—	—	—	—	1
Fusite	1	1	½	—	1	1	—	2	—	1	—	1	1	*Trace*	*Trace*	—

• In these cases the temperature and the value of the maximum fluidity could not be determined, as with increasing temperature the speed of the paddle accelerated rapidly and eventually became too fast to measure.

Table 3

Coalfield / *Colliery* / *Seam* / *Sample* / *Laboratory No.*	*Yorkshire* *Wharncliffe Woodmoor Nos. 4 and 5 Unit* *Winter* *Vitrain* *9308*	*Clarain* *9309*	*Yorkshire* *Ackton Hall* *Warren House* *Vitrain* *9599*	*Clarain* *9600*	*Yorkshire* *Water Haigh* *Beeston* *Vitrain* *9565*	*Clarain* *9566*	*Yorkshire* *Crigglestone* *Low Haigh Moor* *Vitrain* *9567*	*Clarain* *9568*	*Yorkshire* *Wharncliffe Woodmoor Nos. 4 and 5 Unit* *Top Haigh Moor* *Vitrain* *9310*	*Clarain* *9311*	*Yorkshire* *Aldwarke* *Parkgate* *Vitrain* *9530*	*Clarain* *9531*
Analysis												
Air dried basis												
Moisture	5·1	4·5	8·5	6·4	3·8	3·3	3·1	2·9	2·2	1·8	1·6	1·5
Volatile matter	31·7	35·3	30·2	31·5	34·0	34·4	32·9	35·2	31·8	35·4	33·1	30·4
Fixed carbon	62·6	59·5	59·7	56·6	61·3	60·6	63·0	59·7	65·4	61·8	64·3	66·2
Ash	0·6	0·7	1·6	5·5	0·9	1·7	1·0	2·2	0·6	1·0	1·0	1·9
B.S. Swelling No.	—	3½	—	5	—	6½	—	8½	—	7½	—	4
Gray—King coke type	—	G4	—	F	—	G7	—	G7	—	G8	—	G3
Total sulphur	0·72	0·73	1·12	1·32	0·99	0·93	1·37	1·70	0·94	0·91	1·16	0·82
Carbonates as carbon dioxide	0·12	0·06	0·08	0·20	0·05	0·04	0·10	0·21	0·02	0·04	0·02	0·04
Dry ash-free basis												
Carbon	84·3	84·3	84·0	83·6	85·0	85·5	85·1	84·8	85·6	85·6	86·0	87·7
Hydrogen	5·3	5·5	5·1	5·5	5·4	5·4	5·4	5·5	5·4	5·6	5·4	5·3
Nitrogen	1·8	1·8	1·7	1·7	1·9	1·8	1·8	1·7	1·8	1·8	1·9	1·7
Sulphur	0·8	0·8	1·1	1·1	1·0	0·9	1·1	1·1	0·9	0·9	1·0	0·8
Volatile matter	33·6	37·2	33·6	35·8	35·7	36·2	34·3	37·1	32·7	36·4	34·1	31·5
Plasticity data (Gieseler)												
Initial softening point (°C)	382	389	390	408	400	400	390	397	393	382	385	397
Initial fluid point (°C)	414	412	430	428	416	417	419	419	415	408	417	426
Point of maximum fluidity (°C)	433	434	435	435	436	438	438	436	441	433	440	444
Final fluid point (°C)	446	451	440	442	466	463	465	461	460	453	470	469
Solidification point (°C)	455	458	464	459	474	471	476	469	470	461	483	479
Maximum fluidity (div/min)	52	370	12	17	2 100	2 400	880	920	640	3 800	3 400	1 300
Fluid range (°C)	32	39	10	14	50	46	46	42	45	45	53	43
Petrographic analysis												
Maceral distribution												
Vitrinite	97	88	99	86	98	76	99	82	98	86	100	51
Exinite	2	7	0	5	1	6	1	4	1	5	*Trace*	5
Inertinite	1	5	1	9	1	18	*Trace*	14	—	9	*Trace*	44

Table 3—continued

Coalfield / *Colliery* / *Seam*	*South Wales* *Vivian* *Old Coal*		*South Wales* *Vivian* *Meadow Vein*		*Kent* *Snowdown* *18's Face* *Milyard*		*Kent* *Snowdown* *15's Face* *Milyard*		*South Wales* *Oakdale* *Meadow Vein*		*South Wales* *Pochin* *Meadow*		*South Wales* *Ffaldau* *Gellideg*	
Sample / *Laboratory No.*	*Vitrain* *9401*	*Clarain* *9402*	*Vitrain* *9441*	*Clarain* *9442*	*Vitrain* *9346*	*Clarain* *9358*	*Vitrain* *9345*	*Clarain* *9357*	*Vitrain* *9380*	*Clarain* *9381*	*Vitrain* *9386*	*Clarain* *9387*	*Vitrain* *9397*	*Clarain* *9398*
Analysis														
Air dried basis														
Moisture	1·3	1·1	0·8	1·0	0·9	0·8	1·0	0·9	0·8	0·7	0·8	0·7	0·8	0·6
Volatile matter	29·3	28·0	29·4	30·6	23·3	22·5	21·4	20·7	21·6	20·7	19·5	19·1	17·6	17·2
Fixed Carbon	66·4	64·3	66·5	65·9	74·8	75·2	76·4	77·0	75·5	73·8	77·7	75·9	80·9	80·7
Ash	3·0	6·6	3·3	2·5	1·0	1·5	1·2	1·4	2·1	4·8	2·0	4·3	0·7	1·5
B.S. Swelling No.	—	7½	—	7½	—	9	—	9	—	5½	—	9	—	6
Gray–King coke type	—	G6	—	G9	—	G10–G11	—	G10	—	G6	—	G5–G6	—	G4
Total sulphur	0·93	1·38	0·88	0·77	1·08	1·21	1·01	1·04	0·69	0·62	0·74	0·86	0·56	0·52
Carbonates as carbon dioxide	0·18	1·57	0·21	0·25	0·09	0·07	0·04	0·10	0·22	1·08	0·07	0·53	0·04	0·19
Dry ash-free basis														
Carbon	87·7	87·1	88·4	88·6	89·9	90·0	90·6	90·5	90·6	90·3	91·0	91·2	91·6	91·7
Hydrogen	5·2	5·0	5·4	5·3	4·9	4·8	4·8	4·7	4·9	4·7	4·9	4·7	4·7	4·5
Nitrogen	1·5	1·3	1·7	1·6	1·4	1·4	1·5	1·4	1·6	1·5	1·4	1·5	1·5	1·4
Sulphur	0·8	0·7	0·9	0·8	1·0	1·0	1·0	0·9	0·7	0·6	0·7	0·6	0·6	0·5
Volatile matter	30·6	30·3	30·7	31·7	23·8	23·0	21·9	21·5	22·2	21·9	20·1	20·1	17·9	17·6
Plasticity data (Gieseler)														
Initial softening point (°C)	377	393	360	360	405	412	411	417	414	413	422	422	428	447
Initial fluid point (°C)	420	422	409	414	432	442	441	452	445	452	455	458	468	469
Point of maximum fluidity (°C)	453	452	454	449	460	470	466	480	477	474	480	479	490	482
Final fluid point (°C)	481	476	483	483	484	496	489	501	501	494	496	498	501	494
Solidification point (°C)	491	487	490	491	490	503	498	511	508	502	504	505	513	505
Maximum fluidity (div/min)	3 500	2 600	>20 000	11 000	1 100	740	520	300	850	300	220	110	65	35
Fluid range (°C)	61	54	74	69	52	54	48	49	56	42	41	40	33	25
Petrographic analysis														
Maceral distribution														
Vitrinite	93	80	98	78	97	93	97	91	94	80	98	80	97	82
Exinite	2	3	1	6	—	—	—	—	—	—	—	—	—	—
Inertinite	5	17	1	16	3	7	3	9	6	20	2	20	3	18

vitrinites, not necessarily reflected in the analysis. It will be recalled that the behaviour of the pure vitrinites from the Top Haigh Moor at West Riding (*Table 1*) led to the same conclusion.

Analysis of an extended series of vitrinites

Analysis of vitrinites from vitrain bands was extended to a number of other coals, mainly from other British coalfields. In each case the starting material was selected lumps of freshly won coal, from which the vitrain bands were picked out. The associated clarains were also analysed. The results are set out in *Table 3*. The main value of the table is that it presents a series of reliable analyses of clean high-rank vitrains. The associated clarains are included for the sake of completeness; they are, however, petrologically more complex than those in *Table 2* and, furthermore, distinction between vitrinite and exinite is extremely difficult and uncertain at levels of rank above 90 per cent carbon. For these reasons it is not valid to draw conclusions as to whether or not any part of the differences within a pair of samples is due to differences in the vitrinites contained in them.

DISCUSSION OF RESULTS

Figure 1 shows graphically the relationship between carbon and hydrogen (both on dry ash-free basis) for all the vitrinites examined. The relationship

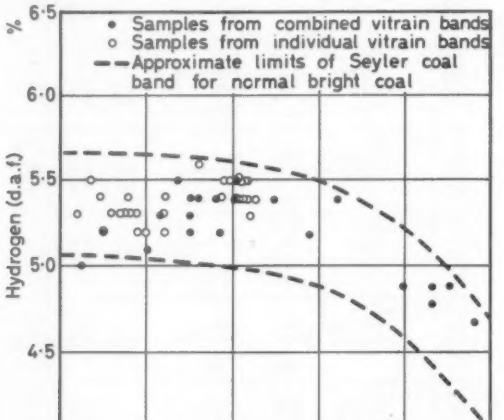

Figure 1. Hydrogen content of vitrinites

between carbon and volatile matter is similarly depicted in *Figure 2*. In each case the approximate limits of the Seyler coal band for normal bright coals are indicated to facilitate comparison between those coals and vitrinites. The data for vitrinites have not been corrected for petrographic inhomogeneity—in most cases the samples contained over 95 per cent vitrinite, the exinite and

inertinite comprising the impurities would demand corrections in opposing senses, and the inaccuracy due to these impurities is thus very small.

For vitrinites containing more than 86·5 per cent carbon the data are not sufficiently numerous to justify any quantitative statement about variability, but it is obvious that below that rank level the spread of values found in the vitrinites is only slightly less than that found in normal bright coals of which the analyses form the basis of the Seyler classification.

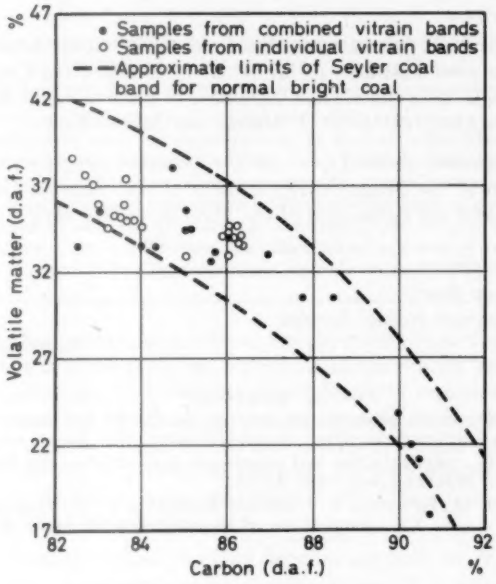

Figure 2. Volatile matter of vitrinites

It is thus opportune to question the conclusions of D. W. VAN KREVELEN[3] that 'from petrographic examinations (percentages of macerals and reflectance measurements on vitrinite under cedar oil) the whole ultimate composition of the coal can be calculated. . . . The same is true for the proximate analysis' and that vitrinite of a given rank has a fixed composition (deduced from the statement that 'it is thus clear that exinites, unlike vitrinites and micrinites, can have different compositions for a given rank'). The uncertainty in the estimation of the carbon content of vitrinite from reflectance measurement is by no means negligible, the correlation between carbon content and either volatile matter or hydrogen is shown above to be far from exact for vitrinites, and, using van Krevelen's data, is even less exact for exinites and micrinites. The combined effect of the uncertainties permits a level of error in the estimation sufficient to render them little better than intelligent guesses.

These findings, while carrying a warning of the dangers of oversimplification, do not in any sense detract from the thesis that coal systematics can be

usefully refined by taking cognizance of and evaluating petrographic complexity. Although the differences found within the vitrinite group are not negligible, they are much smaller than those between the vitrinite group on the one hand and either the exinite or inertinite group on the other. There can be no doubt that the approach adopted in the research mentioned at the outset—to study the properties of each group *as a whole* at different levels of rank—is sound, and that the results so far obtained are convincing demonstrations of the value of quantitative petrographic analysis to the coal scientist.

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Chemical Structure and Properties of Coal XXII—Behaviour of Individual Macerals and Blends in the Audibert–Arnu Dilatometer

D. W. VAN KREVELEN, H. N. M. DORMANS and F. J. HUNTJENS

The percentage swelling ('dilatation') of vitrinite and exinite concentrates and of blends of softening and non-softening coals was measured with the Audibert–Arnu dilatometer. A study of the results has led to the conclusion that there exists a definite correlation between the percentage dilatation and the content of inert constituents. The dilatation of pure vitrinites and exinites was derived from experimental data. The collective body of data now available enables the dilatation of any type of coal to be calculated from the petrographic analysis (rank and maceral analysis). Furthermore, the dilatation of mixtures of several coals can now be calculated if the dilatations of the separate components are known.

PERHAPS the method most widely followed at the present time for studying the coking properties of coals is the measurement of the fluidity and the rate of loss of weight on heating. Only the loss of weight can be measured accurately; an exact determination of the fluidity is made difficult by the concurrent evolution of gas[1]. Since, however, the rate of loss of weight and the fluidity determine the swelling properties of the coal, the measurement of these by means of e.g. the Audibert–Arnu dilatometer[2] provides a reliable procedure for assessing the coking properties.

The dilatation characteristic of a coal depends not only on the rank but to a large extent also on the petrographic composition. The literature already contains data relating the dilatation to the petrographic composition. H. HOFFMANN and K. HOEHNE[3] and K. PATTEISKY[4] made an extensive study of the dilatation of the lithotypes: vitrain, clarain, durain and fusain.

Vitrains in the bituminous range show a characteristic dilatation. Fusain does not soften and, in consequence, cannot swell. As to the dilatation of clarains and durains, however, no unambiguous conclusions can be drawn from the investigations, the reason being that these lithotypes are not homogeneous, but contain several constituents. The composition fluctuates considerably.

The homogeneous components of the lithotypes are the macerals. It will be obvious therefore that a quantitative interpretation of the dilatation characteristic of a given coal cannot be made unless data have been collected about the dilatation of the pure macerals. C. KRÖGER and co-workers[5] succeeded in isolating the macerals vitrinite, exinite and micrinite in a pure state from coals of different rank, and measured *inter alia* the dilatation of these macerals. It appeared that micrinites neither soften nor swell. Exinites equal in rank to

vitrinites with 83·5 and 85·7 per cent carbon show a fluido-plastic behaviour; they soften to such a high degree that, after initial dilatation, the swollen mass collapses again. An exinite of the same rank as a vitrinite with 82·4 per cent carbon is more liable to swell than the vitrinite.

Coke is usually made from coal blends. The component parts of such a blend naturally vary in rank, petrographic composition and particle size distribution. A study by R. BERGER[6] has shown that the dilatation of blends is not an additive quantity. This is confirmed by the results of a provisional examination by D. W. VAN KREVELEN and co-workers[7], who demonstrated that the dilatation curve of any given blend can be calculated from the dilatation curves of the individual coals.

In this paper the dilatation of the various macerals of arbitrary rank will be considered; an attempt will be made to find a correlation between the macèral dilatation and the dilatation of coals chosen at random and coal blends.

EXPERIMENTAL PART

Dilatometer test (Audibert–Arnu)

The dilatation measurements were carried out in the Audibert–Arnu dilatometer[2]. This apparatus, schematically shown in *Figure 1*(a), consists of a tube

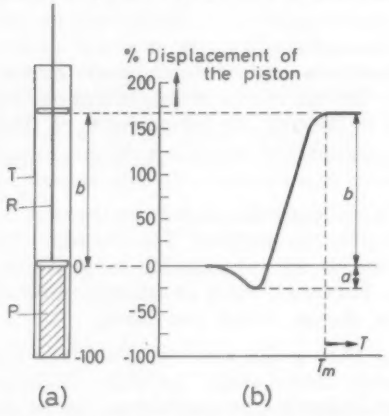

Figure 1. Audibert–Arnu dilatometer and dilatation curve

T in which a piston R can move without friction. Placed between the bottom of the tube and the piston is a pencil of compressed coal. The apparatus is heated at the rate of 3°C per minute. By measuring the movement of the piston as a function of the temperature and expressing it as percentage change of the original pencil length, a graph is obtained of the type shown in *Figure 1*(b). The percentage change in length a is the maximum contraction and b the maximum dilatation; T_m is the temperature at which the dilatation is a maximum.

A deeper study of the dilatometer test reveals that the variation in length b has only a relative and incidental value. This percentage increase in length

Table 1. Dilatation of vitrains

Sample No.	Origin of coal		Maximum reflectance of vitrinite in cedar oil (%)	VM of vitrinite in % (d.a.f.)	Ultimate analysis of vitrinite (d.a.f.)					Maceral analysis % by volume			Max. dil. b (%)	Calculations		
	Seam	Coalfield			C	H	O	N	S	Vitrinite	Exinite	Inertinite		z	z_{V+E}	z_V
1	*Ryder*	*Warwickshire*	0·59	40·8	79·2	5·2	12·9	1·5	0·7	93	3	4	−20	0	0	0
2	*Faulquemont*	*Lorraine*	0·65	41·9	80·2	4·9	13·4	1·2	0·6	90	4	6	−12	0	0	0
3	*Deep Soft*	*Nottingham*	0·66	38·9	81·5	5·2	9·5	1·8	0·6	94	3	3	−16	53	57	40
4	*Beeston*	*Yorkshire*	0·67	37·2	83·7	5·2	8·4	1·9	0·9	100	0	0	−24	0	0	0
5	*Kent's Thick*	*Yorkshire*	0·80	33·4	83·9	5·2	8·0	1·8	0·8	95	2	3	25	127	138	108
6	*Low Beam Shaw*	*Yorkshire*	0·87	35·4	84·2	5·2	7·3	1·8	1·1	96	2	2	79	225	238	216
7	*Lidgett*	*Yorkshire*	1·03	36·0	84·9	5·4	7·1	1·9	1·1	93	3	4	167	385	431	407
8	*Maurits K*	*Limburg*	1·06	32·5	85·2	5·2	6·6	2·0	0·9	93	4	3	77	222	240	177
9	*Maurits M*	*Limburg*	1·06	32·6	85·3	5·2	6·6	1·8	1·1	97	1	2	108	278	296	282
10a	*Haigh Moor*	*Yorkshire*	1·03	33·0	85·6	5·2	6·5	1·3	1·1	100	0	0	83	233	233	233
b	*Haigh Moor*	*Yorkshire*								91	2	7	60	191	234	204
11a	*Maurits D*	*Limburg*	1·15	31	85·8	5·3	5·3	2·1	1·1	82	13	5	308	641	743	587
b	*Maurits D*	*Limburg*								68	27	5	397	804	928	628
12a	*Hendrik D*	*Limburg*	1·09	31	86·9	5·3	4·8	1·8	1·0	81	9	10	366	747	1000	921
b	*Hendrik D*	*Limburg*								83	2	15	264	561	887	869
13a	*Maurits III*	*Limburg*	1·17	27·0	86·9	5·2	4·6	2·0	1·3	98	1	1	353	724	742	739
b	*Maurits III*	*Limburg*								90	1	9	280	591	769	767
14a	*Hendrik V*	*Limburg*	1·28	28·0	87·8	5·2	3·9	2·1	0·8	87	1	12	284	598	860	857
b	*Hendrik V*	*Limburg*								72	0	28	134	325	821	821
15	*Brockwell*	*Durham*	1·26	28·5	87·9	5·2	5·2	1·7	0·4	89	2	9	310	645	839	831
16a	*Emma III/IV*	*Limburg*	1·40	25·0	88·4	5·0	3·3	2·4	1·0	92	2	6	237	513	606	604
b	*Emma III/IV*	*Limburg*								81	1	18	134	325	567	566
17a	*Emma IX f*	*Limburg*	1·63	20·7	89·8	4·8	2·9	1·8	1·0	97	0	3	102	267	290	290
b	*Emma IX f*	*Limburg*								80	0	20	34	144	268	268
18	*Maurits XVIII*	*Limburg*	1·84	17·9	90·2	4·5	2·8	1·9	0·7	95	0	5	41	156	181	181
19	*Gellideg*	*South Wales*	1·75	18·0	90·4	4·5	3·1	1·8	0·4	87	0	11	40	150	214	214

is by no means an absolute measure because the diameter of the pencil changes during the test. At first the diameter is smaller than the internal diameter of the tube but, as carbonization proceeds, the whole cross section of the tube fills up with the swelling coal mass.

Putting the original tube volume between piston face and bottom equal to 100, it can be calculated from the normalized dimensions of the piston and the internal diameter of the tube that the pencil occupies only 55/100 of the volume. In consequence, an absolute measure of the swelling, i.e. the volume dilatation (z), can be derived from the increase in length b by means of the following formula

$$z = (b + 45)/55 \times 100 \text{ per cent} \quad \ldots . [1]$$

EXPERIMENTS

As pointed out above only the macerals vitrinite and exinite possess swelling properties. Micrinite and fusinite behave as inert substances during carbonization and, in maceral analysis, are included therefore under the name 'inertinite'.

To collect data on the *dilatation of vitrinites*, measurements were performed on vitrinite-rich coals (vitrains) of different rank. The vitrains, obtained by hand-picking, covered the range of rank in which vitrinite may show dilatation. In addition to the maceral composition, the elementary composition and reflectance were determined. A survey of the experimental results is presented in *Table 1*.

To examine *the effect of inert constituents* on the dilatation, binary mixtures were prepared of a vitrain with softening and swelling properties and an inert substance. The inert substances used were: non-softening vitrains (with low and high percentages of volatile matter), fusain and sand (*Table 2*).

Table 2. Binary mixtures of a softening vitrain (A) and an inert substance (B)

Softening vitrain (A) % *VM*	*Inert substance (B)*		*Composition* % *by weight*		*Max. dil. b* (%)	*Calculations*		
	Type	% *VM*	*A*	*B*		*Volume fraction* x_A	*z (eqn 1)*	ϕ_i
36·0	*Vitrain*	13·1	100	0	167	1·00	386 ($=z_0$)	1·00
			90	10	110	0·90	282	0·81
			70	30	33	0·70	142	0·53
			55	45	0	0·55	82	0·39
28·5	*Vitrain*	13·1	100	0	310	1·00	645 ($=z_0$)	1·00
			77	23	141	0·77	338	0·68
			60	40	50	0·60	173	0·44
	Vitrain	40·8	72	28	87	0·72	240	0·52
23·5			100	0	143	1·00	342 ($=z_0$)	1·00
	Vitrain	13·1	55	45	−14	0·55	57	0·30
	Vitrain	40·8	80	20	53	0·80	178	0·65
17·8	*Vitrain*	13·1	100	0	40	1·00	154 ($=z_0$)	1·00
			90	10	13	0·90	106	0·77
26·6			100	0	276	1·00	584 ($=z_0$)	1·00
	Fusain	—	95	5	232	0·96	504	0·90
			80	20	152	0·82	358	0·74
	Sand	—	70	30	160	0·82	372	0·78
			40	60	44	0·57	162	0·48

Table 3. Dilatation of exinite concentrates

Series of experiments	*I*				*II*					*III*						*IVa*		*IVb*	
Components																			
Component A	*Durain Faulquemont (density < 1·25) Vitrinite Lidgett seam*				*Durain Beeston seam (density < 1·25) Vitrinite Keats Thick seam*					*Durain Beeston seam (density < 1·30) Vitrinite Lidgett seam*						*Clarains of Maurits seam*			
Component B	80·2				83·7					83·7						85·8			
% C of the vitrinite in A	84·9				83·9					84·9									
% C of the vitrinite in B	84·9				83·2					87·2						31·0			
% VM of the vitrinite in A	41·9				37·2					36·0									
% VM of the vitrinite in B	36·0				33·4														
Maceral analysis																			
% by volume																			
Vitrinite	—	65	85	100	—	30	60	70	100	—	50	60	70	80	100	68	82	63	97
Exinite	59	21	9	—	84	59	34	25	—	73	37	29	22	15	—	27	13	25	1·5
Inertinite	41	14	6	—	16	11	6	5	—	27	13	11	8	5	—	5	5	12	1·5
Max. dilatation b in %	*Only softening*	35	85	145	*Fluido-plastic*	197	63	7	*Only softening*	108	143	140	146	141	145	397	308	254	195
Result of calculation of the inertinite-free mixture																			
Vitrinite in % by vol.	—	76	90	100	—	34	64	74	100	—	58	67	76	84	100	72	86	72	98
Exinite in % by vol.	100	24	10	—	100	66	36	26	—	100	42	33	24	16	0	28	14	28	2
$\Sigma V+E$ *(equation 3)*	—	252	296	346	—	677	246	114	—	977	582	518	472	409	346	928	743	783	457

The dilatation of exinites is less easy to examine than that of vitrinites. Exinite-rich concentrates can be obtained by crushing coal to a very fine particle size and subsequent separation by the float-and-sink method. Concentrates very rich in exinite may, depending on the rank, produce an abnormal dilatation curve, that is to say the fluidity may be so great that the piston sinks through the softened coal mass. To prevent this, exinite-rich concentrates were mixed with vitrinite.

The results of dilatation measurements and maceral analyses have been compiled in *Table 3*. The experiments referred to in columns IVa and IVb differ from those mentioned in the other three columns in that the separations were not made by the float-and-sink method but by hand-picking of the original clarains.

Since, as stated earlier, coke is usually made from blends of softening coals, an attempt was made at correlating *the dilatation of binary and multiple mixtures* of softening coals with the dilatation of the individual components. The results have been compiled in *Tables 6* and *7* (below).

DISCUSSION OF THE RESULTS

(a) *Influence of inert constituents on the dilatation of vitrains* (*and vitrinites*) (*1*) The influence of inert constituents on the dilatation curve of a vitrain was studied by means of the experimental results given in *Table 2*.

When an inert substance has no effect on the dilatation of the vitrinite (i.e. behaves as a truly inert material), it is to be expected that the volume dilatation of the blend will equal the partial volume dilatation of the vitrinite, in other words

$$z = x_A \times z_0 \qquad \ldots . [2]$$

where z = volume dilatation of the blend, z_0 = volume dilatation of the swelling vitrinite, and x_A = volume fraction of the vitrinite in the blend.

When the dilatation of the blends mentioned in *Table 2* is calculated by means of relationship 2, it appears that the values found do not agree with the experimental ones, the latter being always lower than the former. The difference between the two is greater as the inert concentration is higher. This implies that *the dilatation of softening vitrinites is reduced by the inert substance*.

Through the introduction of an inert factor ϕ_i, which takes account of the depressing effect of inert substances on the dilatation of the softening vitrinite, the following relationship is obtained between the volume dilatations of the softening vitrain (z_0) and the blend (z)

$$z = x_A \times z_0 \times \phi_i \qquad \ldots . [3]$$

The inert factor ϕ_i for the various blends has been calculated and plotted versus the volume-percentage inert (*Figure 2*). The graph distinctly shows the existence of a relationship between the inert factor and the inert concentration. It is surprising that *the inert factor is independent both of the dilatation of the softening vitrinite and of the character of the inert substance*.

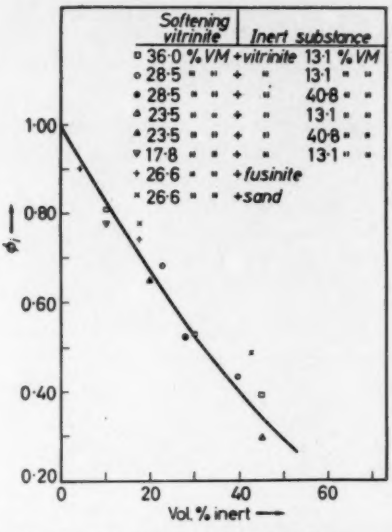

Figure 2. Influence of inert substances on the dilatation of vitrinites

At a given volume concentration inert vitrinites with a high or low content of volatile matter and fusinite influence the dilatation in like manner. Even sand satisfies the above relationship fairly reasonably. To demonstrate the usefulness of the correlation found, the measured and calculated (equation 3) dilatations of the blends mentioned in *Table 2* have been compared in *Figure 3*.

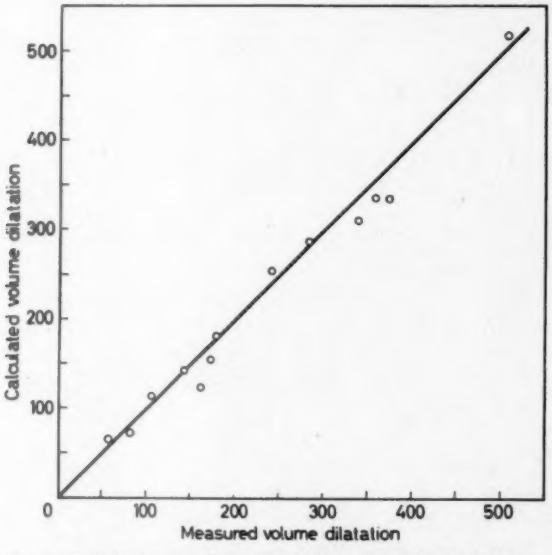

Figure 3. Calculated and measured dilatation of binary mixtures of a softening vitrain and an inert substance

The calculation was carried out solely with the aid of the dilatation of the softening vitrain (z_0) and the curve of *Figure 2*. The good agreement between calculated and measured values confirms the correctness of the method used.

(*2*) In addition to the softening constituents vitrinite and exinite, a softening coal invariably contains inherent inert substances of different character, viz. micrinite, fusinite and minerals. To examine whether these 'inherent inertinites' affect the dilatation in the same way as the inert substances in synthetic binary blends, we measured the dilatation in original vitrains of a given rank containing different amounts of inertinite. The results on these vitrains have been compiled in *Table 4*. The exinite content in all of these

Table 4. Elimination of the influence of inertinite

Sample No. (see Table 1)	VM of the vitrinite in % (d.a.f.)	Maceral analysis % by volume			Max. dil. b (%)	Vol. dil. z (eqn 1)	Vol. dil. z_0 (after elimination of inertinite) (eqn 3)	Deviation %
		Vitrinite	Exinite	Inertinite				
10 *a*	33·0	100	0	0	83	233	233	
b	33·0	91	2	7	60	191	234	−0·4
13 *a*	27·0	98	1	1	353	724	742	
b	27·0	90	1	9	280	591	769	+3·6
14 *a*	28·0	87	1	12	284	598	860	
b	28·0	72	0	28	134	325	821	−4·5
16 *a*	25·0	92	2	6	237	513	606	
b	25·0	81	1	18	134	325	567	−6·4
17 *a*	20·7	97	0	3	102	267	290	
b	20·7	80	0	20	34	144	268	−7·6

samples is very small and negligible. From the dilatation (b and z) of the vitrains, i.e. of vitrinite–inertinite blends, it can be seen that vitrains with a high inertinite content show much less dilatation than vitrains of the same rank but lower inertinite contents.

However, when the effect of the inert is eliminated by means of equation 3, the dilatation values of pure vitrinites (z_0) of the same rank prove to be approximately equal. *This demonstrates that the effect of inherent inertinite can also be very well taken account of by means of the correlation found.*

(*3*) To gain a better insight into the character of the inert factor, we varied the particle size of the inert constituents in some experiments. The inert factor appeared to depend on the particle size of the inert constituents. Its effect on the dilatation decreases with increasing particle size. *Normally, the value of the inert factor ϕ_i is inversely proportional to the total inert surface area.*

This explains why the relationship given in *Figure 2* only holds for the particle size range specified for the Audibert–Arnu dilatometer test. It will also be clear now why in the calculations and in *Figure 2* the amount of inert material has been expressed in volume per cent or as a volume fraction.

(*4*) As the inert surface area determines the value of the inert factor, it will be obvious that the *shape factors* of the inert particles should also be taken into

account. The shape factor indicates the ratio between the surface area of a non-spherical particle and a spherical particle of the same volume. The shape factor of the various substances can be determined microscopically by Heywood's method[8].

In *Figure 4* the shape factors for the inert vitrinites and sand have been brought into the calculations. The difference between sand and inert vitrinites, as observed in *Figure 2*, has now completely disappeared.

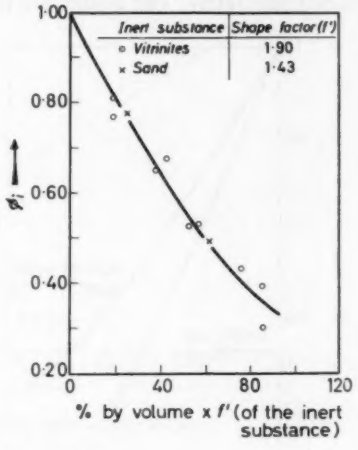

Figure 4. Addition of the shape factor to the correlation ϕ_i versus % inert

(b) *Influence of exinite on dilatation of vitrinite*

(*1*) As stated earlier, coal containing much exinite may show a typical behaviour in the Audibert–Arnu dilatometer. When the piston has reached its maximum height it sinks rapidly, occasionally even down to the bottom of the dilatometer tube (*Figure 5*). This phenomenon is to be ascribed to the fact that the exinite becomes fluido-plastic and to the concurrent, profuse gas evolution.

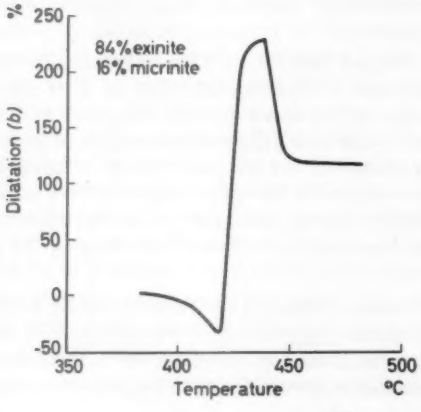

Figure 5. Dilatation curve of a fraction rich in exinite

Below a given exinite content, the shape of the dilatation curve again becomes normal. Most types of coal used in practice have such a low exinite content that the curve shows a normal course.

(*2*) The exinite concentrates mentioned in the columns I, II and III of *Table 3* were obtained from coal which, to permit effective separation into the various macerals, had been crushed to a very fine size. Since, as explained above, the effect of inert material on the dilatation is a function of the particle size, the effect at a particle size equal to that of the exinite concentrates was determined separately. The results are presented in *Figure 6*. It can be seen

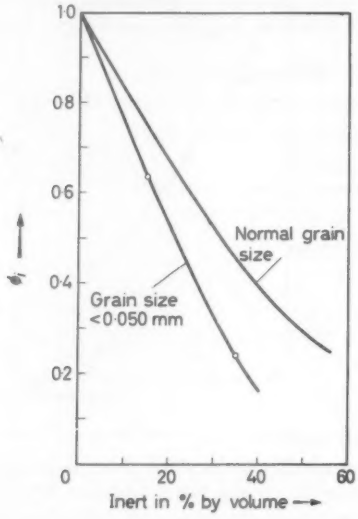

Figure 6. Influence of inerts of different grain size on the dilatation

that the effect of inert material of a given concentration is now greater than in coals of the particle size specified for the dilatometer test. In the mixtures of columns I, II and III of *Table 3* these effects have therefore been eliminated by means of equation 3; the value of the factor ϕ_i in this equation must be read from the lower curve in *Figure 6*.

In the experiments of series IVa and IVb (*Table 3*) the particle size was as specified for the dilatometer test and eliminating the effect of inert material had therefore to be done by means of the upper curve in *Figure 6*. As will be shown later, mixtures of a given exinite with different percentages of inertinite all lead to the same maximum dilatation for the pure exinite. *This confirms the view that inert matter affects exinite in the same way as it does vitrinite.* The volume dilatation of vitrinite–exinite mixtures found by calculation, after elimination—quantitatively and qualitatively—of the effect of the inertinite, is given in *Table 3* (z_{V+E}).

(*3*) *Figure 7* shows how the volume dilatation of vitrinite–exinite mixtures (series III of *Table 3*) varies with the composition. *From this curve it can be seen that in mixtures of vitrinite and exinite of the same rank, the dilatation of the macerals may be considered as a practically additive quantity.*

Thus it is possible to calculate the dilatation of pure exinite from the dilatation of two coal samples from the same seam but with different exinite contents. *Although the value thus found need not have real significance for pure exinite—considering that this may produce an abnormal dilatation curve (fluido-plastic)—it has now become possible to calculate the dilatation of any type of coal of known petrographic composition.*

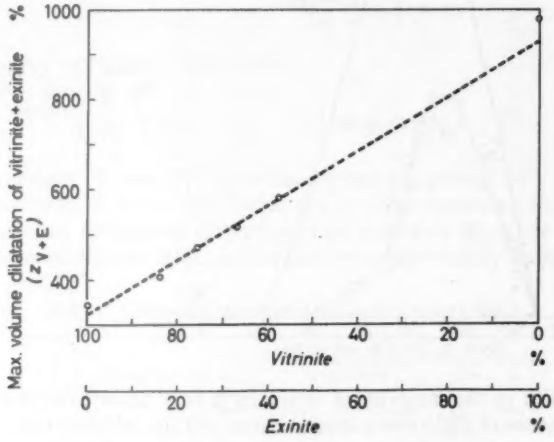

Figure 7. Dilatation of vitrinite–exinite mixtures

(c) *Dilatation of pure macerals*

Now that all correction factors are known, the dilatation of pure exinites and vitrinites can be calculated by means of the derived correlations.

After elimination of the effect of inert matter by means of equation 3, the collective dilatation of vitrinite and exinite (z_{V+E}) has been derived from the dilatations of the exinite concentrates (*Table 3*). As the vitrinite and exinite dilatations are additive, *the dilatation of pure exinites can be found by extrapolation.* In *Figure 8* the results are plotted against rank, the rank being expressed by the carbon content of the corresponding vitrinite. C. KRÖGER[5] measured the dilatation of a number of pure exinites directly. Pure exinite equal in rank to a vitrinite with 88·4 per cent carbon, produces a normal dilatation curve. The maximum dilatation of this curve is also presented in *Figure 8*. From the examination reported in Part XX of this series[9] it appears that vitrinite and exinite of the same rank as vitrinite with about 91 per cent carbon possess the same chemical and physical properties and the same structural parameters. It is very likely therefore that vitrinite and exinite of higher rank will also show the same dilatation. This explains why in *Figure 8* the exinite curve has been traced to the point for vitrinite dilatation.

Now that the exinite curve is known, the dilatation of vitrains (*Table 1*) can be corrected to give the *dilatation of pure vitrinites.*

First the effect of inertinite is eliminated by means of equation 3; this gives the collective dilatation values for vitrinite and exinite (z_{V+E}). The remaining

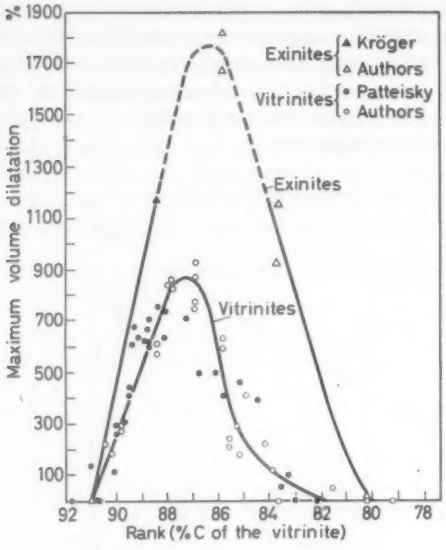

Figure 8. Dilatation of the macerals vitrinite and exinite

exinite, which in the majority of vitrinites is very scanty, can now be eliminated by means of the known exinite curve and the additive rule. The dilatation of pure vitrinites (z_V) thus found is also presented in *Figure 8*. A more extensive study of the maximum dilatation of vitrinite-rich coals was also made by K. PATTEISKY[4]. His dilatation values, in terms of volume dilatation, together with results of the present study are included in *Figure 8*. The agreement is good.

(d) *Dilatation of a coal chosen at random*

The data now available enable a correlation to be made between the results of the petrographic examination and coking properties for any given type of coal.

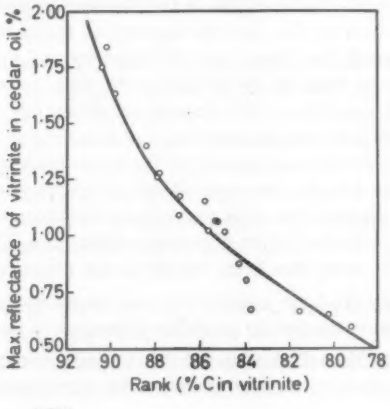

Figure 9. Correlation between rank and reflectance

By means of the microscope and the microphotometer *the maceral concentrates and the reflectance of vitrinite* can be determined. The reflectance is closely related to the *rank* expressed by the carbon content of the vitrinite (*Figure 9*). The results refer to the vitrinites of *Table 1*. For calculating the volume dilatation from the results of the petrographic analysis, the following relationship can be derived

$$z = \left(\frac{V}{100} \times z_V + \frac{E}{100} \times z_E\right) \times \phi_i \qquad \ldots . [4]$$

Combination of equations 1 and 4 gives

$$b = \left(\frac{V}{100} \times z_V + \frac{E}{100} \times z_E\right) \times \phi_i \times \frac{55}{100} - 45 \qquad \ldots . [5]$$

In these equations: V and E denote the volume percentage of vitrinite and exinite respectively, ϕ_i is the inert factor at I per cent inertinite, z_V and z_E are maximum volume dilatations of vitrinite and exinite of the given rank, and b is the maximum volume dilatation of the coal under test in length per cent.

Table 5. Calculated maximum dilatation of some coals

Origin of the coal	*Reflectance vitrinite in cedar oil %*	*% C from Figure 9*	*Maceral analysis % by volume*			*Volume dilatation z, %*		*Dilatation b, %*	
			Vitrinite	*Exinite*	*Inertinite*	*Calculated (eqn 4)*	*Measured*	*Calculated (eqn 5)*	*Measured*
Lorraine	0·89	84·0	58	20	22	191	346	60	145
Maurits D (Limburg)	1·15	86·9	66	14	20	535	503	249	232
Maurits III (Limburg)	1·27	87·9	73	7	20	469	463	213	210
Maurits VII (Limburg)	1·44	89·0	76	2	22	270	256	103	96
Maurits XVI (Limburg)	1·82	90·6	70	0	30	37	95	−25	7

The results, calculated for some coals chosen at random and used in practice, have been compiled in *Table 5*. Note the large difference between the calculated and measured dilatations of coal with 84·0 per cent carbon. An explanation for this phenomenon might be found in the well known fact that coals from the Lorraine may contain submicroscopic resin inclusions. Moreover, it should be borne in mind that in the range of rank considered here the dilatation is not an unambiguous function of rank. The deviation for coal with 90·6 per cent carbon is also large. However, a small difference in carbon content in this range of rank causes a large relative change in the dilatation of the vitrinite. The calculated and measured dilatations of the other three coals, which cover the range between 86 and 90 per cent carbon, agree very well.

(e) *Dilatation of mixtures of coals of different rank*

(*1*) In practice much use is made of the Audibert–Arnu dilatometer for characterizing coal blends according to their suitability for the production of coke. For the purpose of this characterization it is important to investigate how the dilatation of a mixture can be correlated with the dilatation of the components. *Figure 10* (a) to (f), in which the experimental results are presented, shows how the dilatation of binary vitrain blends varies with the

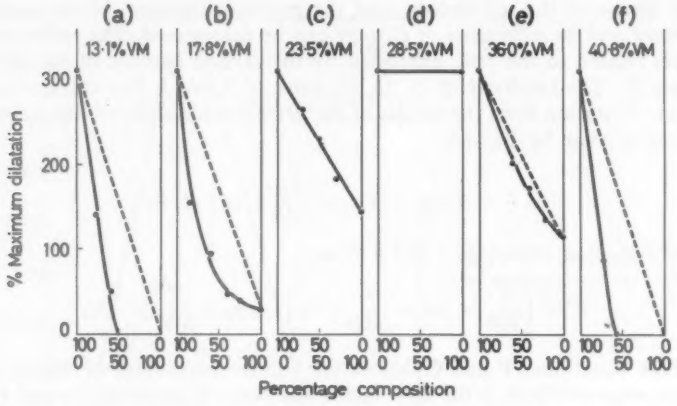

Figure 10. Maximum dilatation of binary mixtures of a vitrain with 28·5 per cent volatile matter and a vitrain of another rank

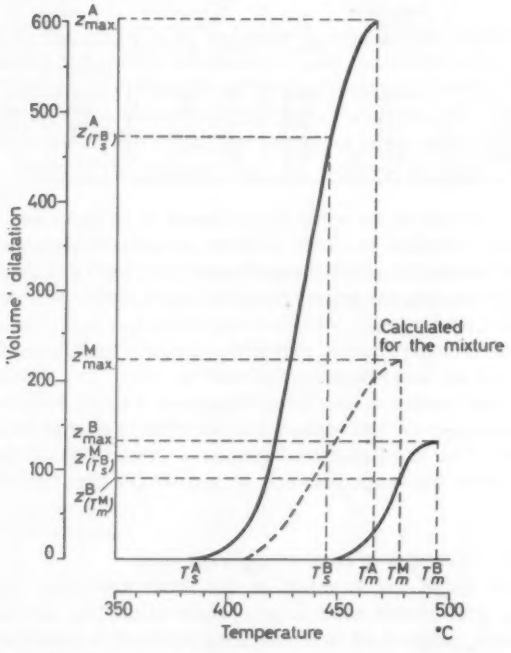

Figure 11. Calculated dilatation curve of a mixture of 60 per cent A and 40 per cent B, where A and B have respectively 28·5 and 17·8 per cent volatile matter

blending ratio. One of the components is always the same type of coal with 28·5 per cent volatile matter. From the figure it can be seen that the dilatation of binary mixtures is usually not an additive quantity. The deviation from the additive rule increases with the difference in rank between the two components, and becomes a maximum when one of the components is an inert material. The dilatation of the mixture in the latter case can be calculated by means of equation 3.

(*2*) The non-additive nature of the dilatation of vitrains of different rank can be explained by the fact that coal having a higher softening point has a diminishing effect on the dilatation of coal with a lower softening point. In *Figure 11* we have traced the volume dilatation curves for two coals A and B with 28·5 and 17·8 per cent volatile matter respectively. The curves were derived from the normal curves by means of equation 1 (see *Table 6*). To enable the dilatation of such binary mixtures of softening coals to be calculated, the temperatures must be known at which the various coals change from the solid into the plastic state (T_s). By trial and error it has been found that the temperature at which the coal in the dilatometer shows 10 per cent

Table 6. Dilatation of binary mixtures of softening vitrains

Volatile matter %		*Composition % by weight*		*Max. dil. (b) %*
Component A	*Component B*	*Component A*	*Component B*	
28·5	36·0	100	0	286
		60	40	187
		40	60	160
		20	80	130
		0	100	114
28·5	23·5	100	0	286
		70	30	248
		50	50	219
		30	70	176
		0	100	143
28·5	17·8	100	0	286
		85	15	134
		60	40	81
		40	60	37
		25	75	33
		0	100	29
23·5	17·8	100	0	143
		75	25	76
		60	40	56
		40	60	38
		25	75	32
		0	100	29
36·0	17·8	100	0	167
		84	16	96
		68	32	37
		46	54	16
		23	77	22
		0	100	39

contraction is the most suitable. In *Figure 11* these temperatures are indicated as T_s^A and T_s^B.

The temperature at which the dilatation of a mixture is maximum (T_m^M) can, as a first approximation, be derived from the corresponding temperatures of its components by means of the following equation

$$T_m^M = x_A \times T_m^A + x_B \times T_m^B \quad \ldots . [6]$$

where x_A and x_B denote the fractions of which the mixture is composed. *In the temperature range $T_s^A - T_s^B$ only component A shows swelling whereas component B behaves as an inert substance.*

From equation 3 it follows therefore that at temperature T_s^B the dilatation of the mixture ($z^M_{(T_s^B)}$) amounts to

$$z^M_{(T_s^B)} = z^A_{(T_s^B)} \times x_A \times \phi_i \quad \ldots . [7]$$

In the temperature range $T_s^B - T_m^M$ the two components are soft and the dilatation of the mixture equals the sum of the partial dilatations of the components within this temperature range.

$$z^M_{(T_s^B \rightarrow T_m^M)} = x_A(z^A - z^A_{(T_s^B)}) + x_B \times z^B_{(T_m^M)} \quad \ldots . [8]$$

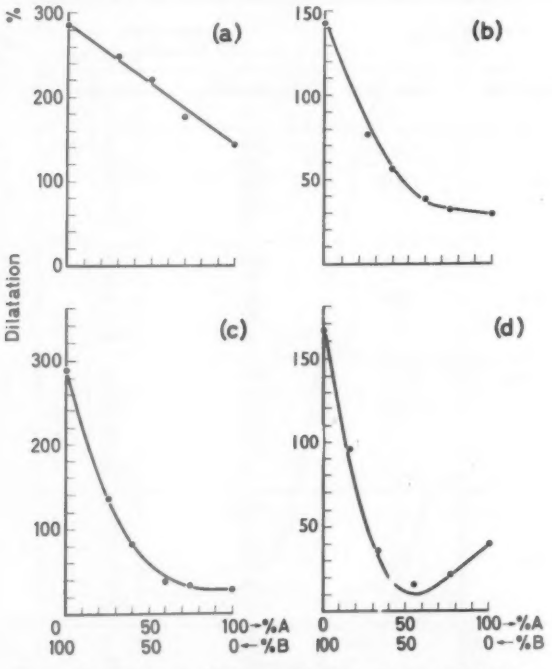

Figure 12. Maximum dilatation of binary mixtures of vitrains. ——— Calculated curves; ● measured values. (a) *Mixture contains A with 23·5 per cent volatile matter and B with 28·5 per cent volatile matter;* (b) *A = 17·8 and B = 23·5;* (c) *A = 17·8 and B = 28·5;* (d) *A = 17·8 and B = 36·0*

In consequence, the maximum dilatation of the mixture equals the sum of the dilatations calculated by means of equations 7 and 8

$$z_m^M = z_{(T_g^B)}^M + z_{(T_g^B \rightarrow T_m^M)}^M \quad \ldots . [9]$$

The results calculated for binary mixtures are shown in *Figure 12*. The drawn curves have been calculated by means of equation 9; the points indicate the experimental values. The agreement is very good.

(*3*) The dilatation of a mixture of more than two components can be determined in a similar manner. The contribution to the total dilatation is carried out in stages extending between the successive softening temperatures of the components, bearing in mind that components of higher softening temperature affect the dilatation of components of lower softening temperature in the same way as inert substances.

Table 7. Mixtures of five components

	Composition %					*Volatile matter %*	*b-dilatation*	
	I	*II*	*III*	*IV*	*V*		*Meas.*	*Calc.*
Components	100	—	—	—	—	17·6	0	—
	—	100	—	—	—	19·6	39	—
	—	—	100	—	—	23·5	143	—
	—	—	—	100	—	26·6	275	—
	—	—	—	—	100	29·7	261	—
Mixtures	10	18	40	22	10	—	90	92
	31	13	10	17	29	—	39	28
	20	20	20	20	20	—	59	55
	14	16	23	22	25	—	96	89
	24	22	20	18	16	—	41	37

The calculated and measured dilatation values for a number of multiple mixtures are presented in *Table 7*. Here also the agreement is very good.

CONCLUSIONS

(*1*) During examination in the Audibert–Arnu dilatometer pure vitrinite and exinite produce very characteristic and reproducible dilatation curves; these dilatations vary with the rank (*Figure 8*). Micrinite and fusinite neither soften nor swell ('inertinites').

(*2*) The dilatation of a mixture of vitrinite and exinite of the same rank equals the sum of the dilatations of the separate components.

(*3*) Inertinites reduce the dilatation of vitrinite and exinite in accordance with a generally valid correlation which depends only on the particle size and the external shape ('shape factor').

(*4*) Coals of different rank occurring in a blend behave as partially inert substances. The behaviour of such a blend can be calculated.

(*5*) The thermal behaviour of any coal or coal blend can be completely interpreted by means of the petrographic analysis (i.e. by maceral and rank analysis) and the knowledge of the behaviour of the individual maceral.

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Characterization of Pitches for Carbon Anodes

M. B. DELL

Pitches were analysed for the usual determinations including coking value, C-I, C-II, *and atomic* C/H *ratio. Relative aromaticities of the pitches were also measured by refractive index and sulphonation index of pitch distillates,* C/H *ratio of the carbon disulphide soluble phase, and infra-red index. The relative aromaticities agreed quite well among themselves but did not correlate with the usual determinations. It was shown that the density and reactivity of carbon anodes varied with the aromaticity of the binder pitch as measured by infra-red index.*

NUMEROUS tests have been suggested for characterizing the binder pitches that are used in anodes for aluminium smelting. The commonly employed ones include softening point, ash content, coking value, and the amount of material insoluble in quinoline, benzene, or acetone. Some of these measure utility rather than quality. Softening point determines the minimum mixing temperature of the coke–pitch blend; ash content affects the purity of the aluminium. Other of these tests are indirect measures of aromaticity in the oil phase. D. W. VAN KREVELEN and H. A. G. CHERMIN[1] have pointed out that aromatic compounds form coke more readily than non-aromatic compounds. Accordingly, the coking value of pitch is really an indirect measure of aromaticity. Similarly, for coke-oven pitches, a high C-I content shows that the pitch is highly cracked and more likely to have a high aromatic content.

Recently, new tests have been proposed to characterize binder pitches. H. BRÜCKNER and G. HUBER[2] recommended solvent fractionation. V. N. KRYLOV *et al.*[3] investigated the 'free carbon' fraction. S. W. MARTIN and H. W. NELSON[4] suggested a modified coking value test and also[5] the use of specific gravity corrected for C-I. L. P. CHARETTE and G. T. BISCHOFBERGER[6] found a good correlation between compressive strength of a carbon anode, and the product of coking value and carbon/hydrogen ratio of the pitch binder. D. S. MONTGOMERY and F. E. GOODSPEED[7] discussed infra-red (i.r.) spectroscopy of binder pitches using the KBr technique.

In the work reported here, binders representing different types of pitches were analysed by the usual characterizations and by tests which measure their aromaticity. These latter tests comprised carbon/hydrogen ratio of the whole pitch, carbon/hydrogen ratio of the carbon disulphide-soluble phase, sulphonation index, refractive index, and i.r. index. As will be shown, aromaticity of the binder pitch is important for carbon anodes used in aluminium smelting.

In comparing pitches by these tests, the composition of pitch should be kept in mind. Pitches consist of an insoluble phase suspended in an oil phase.

Insoluble matter is derived chiefly from the soot formed during thermal cracking of tars from which pitches are produced, and from carry-over of the material being carbonized. The oil phase consists chiefly of hydrocarbons sometimes with the presence of compounds containing oxygen, sulphur, or nitrogen. No single chemical compound predominates in the oil phase.

The amount of material insoluble in certain solvents is usually designated C-I when a good solvent such as carbon disulphide or quinoline is used. C-II designates the difference between the material insoluble in a poor solvent such as acetone or benzene and the C-I. E. J. DICKINSON[3] demonstrated that the C-I fraction corresponds to the tar-insoluble matter, and that the C-II fraction contains the higher molecular weight substances of the oil phase.

PROCEDURE

Softening point was determined by the cube-in-air method, Barrett D-7.

Coking value was determined by method *ASTM D–271* in which a 1 g sample is heated to 950°C for seven minutes in a platinum crucible.

C-I—A 0·5 g sample of the binder was digested in 10 ml of quinoline for 30 minutes at 70° to 80°C. The solution was filtered hot, washed with ten 5 ml portions of quinoline, and twice with benzene. The insoluble matter was weighed and reported as C-I.

C-II—100 ml of acetone was added slowly to a 0·5 g sample of binder, then stirred and filtered with suction through a Royal Berlin porcelain crucible, type 1A2. Insoluble matter was washed once with 10 ml of acetone, dried, weighed, and reported as C-I plus C-II. The C-II value was the difference between C-I and the acetone-insoluble.

Sulphonation index and refractive index—Each binder was distilled in a side-neck Church flask using the procedure of *ASTM D–20*. The 300° to 365°C fraction was retained for determination of both the sulphonation index and refractive index. Sulphonation index was determined by method *ASTM D–872* as the ml of unsulphonated residue per 100 g of distillate using 37N sulphuric acid. Refractive indices were determined at 25°C for solutions in *p*-xylene containing 25 per cent distillate.

Atomic carbon/hydrogen ratio—C/H was calculated from the carbon and hydrogen content of the pitch, determined in a combustion train.

Atomic carbon/hydrogen ratio of the carbon disulphide soluble phase—5 g of pitch was dissolved in 20 g carbon disulphide, filtered through a medium sintered-glass filter, and washed four times with a total of 20 g carbon disulphide. Carbon disulphide was evaporated from the combined filtrates in a warm Petri dish. Carbon and hydrogen were determined on the extract.

Infra-red index—Exactly 0·25 g of pitch was dissolved in 10 ml of carbon disulphide and allowed to stand 2 h; then the i.r. spectrum of the supernatant liquid was determined, using a cell width of 0·50 mm in a Perkin–Elmer Model 112 spectrometer. After correcting for the absorption of the solvent, the i.r. index was taken as the ratio of the aliphatic transmittance at 3·4 microns divided by the aromatic transmittance at 3·3 microns. It was realized

that absorption might be used instead of transmittance, but since the index is an arbitrary ratio, the transmittance was used because the calculations were somewhat simpler. Aliphatic and aromatic transmittances at other wavelengths could have been used, but they produce little change in the relative indices of a series of pitches.

DISCUSSION AND RESULTS

The importance of aromaticity of simple binders in determining the quality of carbon anodes is shown in *Figure 1*. With increasing aromaticity, the baked

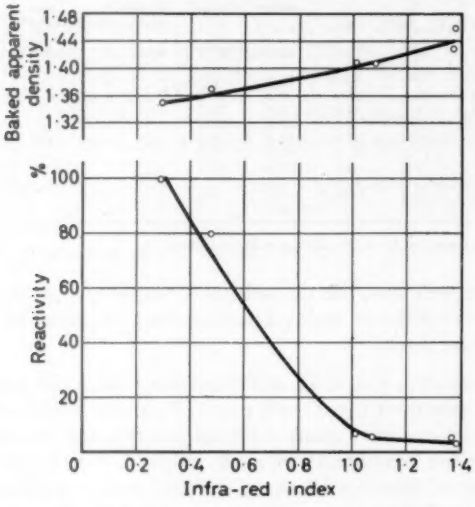

Figure 1. Effect of binder aromaticity on properties of anodes

apparent density of the anode increases. At the same time, the reactivity of the anodes decreases. The reactivity was taken as the loss in weight on immersing a 1 in. cylinder of carbon, 0·5 in. long, for 30 minutes in sodium sulphate at 980°C.

In *Table 1*, results of the analytical determinations are tabulated for a variety of pitches. The pitches are arranged in decreasing order of i.r. index with the most aromatic pitch at the top. The i.r. index increases regularly with C/H of the carbon disulphide soluble phase. It is a particularly sensitive measure of pitch aromaticity at high C/H ratios.

The deceptiveness of C/H of the whole pitch, as a measure of aromaticity, is illustrated by the horizontal retort pitch where C/H of the whole pitch did not correspond with i.r. index or the C/H of the carbon disulphide soluble phase. This is explained by the fact that the large amount of C-I having a high carbon content in this pitch tended to counteract the high hydrogen content of the oil phase.

The refractive index of the distillate fraction in *p*-xylene gave values that were somewhat indicative of the relative aromaticity of the pitch, but the results did not agree as well with the i.r. index or the C/H of the soluble phase

The sulphonation index of the distillate fractions agreed quite well with C/H ratio. The determination, however, is difficult to perform, and the test lacks sensitivity. The i.r. indices of the 300° to 365°C distillate fractions

Table 1. Characterization of pitches

Type	Softening point °C	C-I %	C-II %	Coking value	Coking value minus C-I	Atomic C/H		Sulphonation index*	Refractive index*	Infrared index	Infrared index*
						Whole pitch	CS_2 sol phase				
Coke oven A	109	16·5	33·0	44·1	27·6	1·91	1·77	0·0	1·5352	1·38	1·41
Coke oven B	109	7·6	32·0	—	—	1·77	1·72	0·0	1·5376	1·37	1·38
Coke oven C	110	13·7	30·8	44·2	30·5					1·35	
Horiz. retort	108	29·6	25·4	58·8	29·2	2·12	1·70			1·29	
European (?)	104	11·5	24·8	35·2	23·7	1·71	1·67			1·08	
Oil-gas A	116	13·3	37·2	42·8	29·5	1·74	1·59	2·2	1·5279	1·01	0·61
Water-gas	115	17·4	33·5	54·4	37·0	1·66	1·49	4·7	1·5298	0·94	0·59
Oil-gas B	114	17·0	27·1	50·7	33·7					0·83	
Low temp.	87	0·2	4·6	11·1	10·9	1·15				0·47	
Lignite	—	2·8				0·81			1·5000	0·15	
Gilsonite	147	0·0	90·5	17·2	17·2	0·77	0·75			0·05	

*These determinations were made on the 300° to 365°C distillate.

correlated quite well with the i.r. indices of the whole pitch. This is understandable because in the i.r. index determination the spectrum is only that of the oil phase of the pitch.

The traditional tests, C-I, C-II, and the coking value did not correlate with aromaticity as measured by i.r. index or C/H of the soluble phase. The C-I phase of the pitch can have many different sources, and its amount does not necessarily measure aromaticity of pitch. While C-I, C-II, and coking value make good control tests for checking the uniformity of different shipments of pitch, their usefulness in evaluating new pitches is quite limited. The coking value, while it is in part a measure of the aromaticity of the pitch, is also affected by the insoluble content of the pitch. For example, the horizontal retort pitch that had a relatively low i.r. index had a high coking value. Apparently this high coking value was mainly due to the high C-I content, which on carbonization goes almost entirely to form coke.

The coking value minus C-I, which has sometimes been suggested as a characterization factor for pitches, again shows no correlation with the aromaticity of the pitches as determined by i.r. index or C/H of the carbon disulphide-soluble phase.

CONCLUSIONS

The quality of carbon anodes is related directly to the aromaticity of the binder pitch. The usual tests for pitches such as C-I, C-II, and coking value do not correlate with aromaticity.

The more useful characterizations for aromaticity include the C/H of the carbon disulphide-soluble phase, sulphonation index, and i.r. index of the whole pitch and the distillate fraction. Of these, the one that is most quickly

determined is the i.r. index of the whole pitch. The determination requires less than half an hour. Such a test should find wide application in laboratories that are called to examine numerous types of pitches.

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Studies in Bomb Calorimetry X— Conditions for the Combustion of Solid and Liquid Fuels

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The use of a sensitive method for determining carbon monoxide in the residual gases of a calorimetric bomb showed that appreciable quantities of carbon monoxide occurred, even without traces of residual carbon, particularly for fuels which, after extinction of the flame, left a residue of carbon, e.g. coke, anthracite, benzene and gas oil. The use of a Window Bomb enabled the flame period and the total combustion period to be measured, and a selection of crucibles of various top diameters to be made to make these combustion characteristics approximately the same for most fuels. Increase of the initial pressure of oxygen to 30 or 35 atm (with a drop of added water for the least reactive fuels) enabled the carbon monoxide to be reduced to be below 30 p.p.m. and so removed a major factor causing poor repeatability. Reduction of the top diameter of the crucible enabled the combustion period of fast-burning fuels to be slowed down, so that dangerous pressures could never be produced; this, and the control of the initial pressure of oxygen, gave both good repeatability and conditions for standard combustion characteristics of benzoic acid and most fuels (desirable in obtaining identity of thermal conditions in the determination of effective heat capacity and of calorific value). The conditions for determination of the effective heat capacity need modifying only in that, if the Griffin–B.C.R.A. Isothermal Bomb Calorimeter is to be used for coke and other unreactive materials, the length of chief period should be 10 min. The use of nickel–chromium crucibles, with a flange for support in a ring attached to the non-insulated pole of the bomb and which enables a disc of Sellotape to be affixed to seal volatile liquids, gives an improved method for dealing with liquid fuels.

It has been emphasized in Parts I[1], II[2] and III[3] of this series that a primary requirement in the determination of the calorific value of a fuel is that complete combustion of the sample shall be ensured. It is also desirable that the combustion period should be the same for the fuel as for the benzoic acid used for the determination of the effective heat capacity of the calorimeter. The reason for this latter desideratum is the fact that, in work of high accuracy, it is necessary to take special steps to ensure that small but significant differences do not arise between the effective heat capacity which actually obtains and that which has been determined and which is to be used in the calculation of the calorific value of the fuel. This matter has been discussed in Parts VII[4] and VIII[5], the conclusions reached being that the length of the chief period in the standardization of the calorimeter should be so chosen as to give the best repeatability, that the total heat release in the determination of calorific value should be approximately the same as in the standardization (as advised in Part III[3]), that the combustion periods of the fuel sample and the benzoic acid should be approximately equal, and that the length of the chief period should be the same as in the standardization. In essence, then, the ideal to be aimed at may be called 'identity of thermal conditions' in the

two determinations. The present paper describes work carried out to show how this identity may be achieved.

In Part VIII[5] it was suggested that it might be possible to modify the burning characteristics of benzoic acid to comply with those of a variety of types of solid and liquid fuels. In fact, it has been found more profitable to study the modification of the burning characteristics of the fuels to comply with those of benzoic acid; if this could be done for all types of solid and liquid fuels, whilst not impairing the completeness of combustion, the necessity for multiple standardization of the calorimeter would be overcome. Thus the desiderata are that the combustion of slow-burning fuels—such as coke—shall be speeded up and that the combustion of fast-burning fuels—such as aviation spirit—shall be slowed down. It should be mentioned here that, to obtain control of the combustion period of samples of liquid fuels, it was found necessary to adopt a method of containing the samples different from that described in Part II[2] of this series. In that this new method gives a much lower chance of a wasted determination due to incomplete combustion of a very fast-burning material such as *iso*pentane, it is recommended for general adoption. This does not materially affect the conclusions which were drawn in Part II[2] about the maximum pressures likely to be developed: as the new method (under defined conditions) gives increased combustion periods, the maximum pressures are likely to be less, so that those previously derived still form a safe basis for the design of calorimeter bombs. Thus the new method can be applied without fear in bombs which conform to the principles of design and construction laid down in Parts V[6] and VI[7].

Briefly, control of the rate of combustion of different fuels is obtained by varying the top diameter of the crucible used, an increased diameter giving an increased rate for a given fuel. By means of this simple device, it is possible to slow down the combustion of such a fast-burning material as *iso*pentane so that explosive combustion is prevented and there is no danger of an excessive maximum pressure being produced. For some liquid fuels, for example paraffin hydrocarbons, the period of duration of the flame is the same as the total combustion period; for others, for example benzene, the combustion period is longer than the flame period due to the necessity for burning-off a carbonaceous residue, a feature common to all solid fuels. For paraffin hydrocarbons it will be shown to be desirable to slow down the combustion, but this tends to leave some carbon monoxide in the residual gases; this can be overcome by increasing the initial pressure (P_i) of oxygen, a device also necessary for increasing the rate of combustion of such a slow-burning fuel as coke. Thus the attainment of the optimum conditions for calorimetry requires a balance between crucible top diameter and initial pressure of oxygen. Since the total combustion period is not itself a sufficiently distinctive parameter, it is necessary to use others to assess the optimum conditions. For this purpose, T_m, the period for 60 per cent of the total temperature rise to occur (Dickinson cooling correction), and n, the length of the chief period (the end-point being chosen in accordance with the rules laid down in Part III[3]), have been favoured. It has also been required that the chosen conditions shall give a low standard deviation for the results of a series of six determinations.

INCOMPLETE COMBUSTION

In Part I[1] it was shown that visibly complete combustion of slow-burning ('unreactive') materials, natural graphite, artificial graphite and anthracite, could be ensured, without any addition of a 'fuse' of paper or benzoic acid, etc., by spreading the sample in a 1½ in. diameter crucible on a layer of fine, granular alumina. It was also shown that, for a wide range of bituminous coals, durain, lignite, peat and torbanite, briquetting was undesirable (encouraging ejection of particles) and visibly complete combustion was attained either by using the same conditions as for the unreactive materials or by simply using a 1 in. diameter crucible. All the tests were carried out using a bomb of only 250 ml capacity and an initial oxygen pressure of 25 atm (gauge). Nickel–chromium crucibles were preferred to silica crucibles, though it was recorded that tests in another laboratory had shown that the use of a silica crucible in a bomb of 350 ml capacity overcame the tendency for smudges of carbon to be produced when testing high-volatile coals.

In the same paper[1] it was shown that benzoic acid could not be burnt loose owing to ejection of material: either briquetting or melting is necessary to increase the bulk density. In Part III[3] it was shown that a nickel–chromium crucible of very low mass was desirable to ensure visibly complete combustion of the quantity (1·2 g) which it is normally wished to burn in each determination of effective heat capacity.

In Part II[2] a method for burning gas oil, gasoline, benzene and aviation spirit was described; this involved the use of the 1 in. diameter nickel–chromium crucible (the 'coal crucible'), with a No. 000 gelatine capsule (to hold the sample) resting on a bed of fine, granular alumina of defined thickness. With a bomb of 250 ml capacity and an initial oxygen pressure of 25 atm (gauge), this method was satisfactory provided that the heat release was limited to 25 cal per ml of bomb capacity. For *iso*pentane, this same limit had to be applied, but a thinner nickel–chromium crucible was desirable and the initial oxygen pressure had to be raised to 32·5 atm (gauge); even then, there was only a roughly 50 per cent chance of visibly complete combustion being achieved. The pressures which may arise when using this method were investigated by the British Petroleum Co. Ltd, the results being reported, and applied to the problem of bomb design, in Part V[6]. The virtue of the method was that the tendency for excessive pressures was overcome.

Although 'visibly complete combustion' (the presence of no unburnt carbon in the crucible or on the bomb walls or cap) must be the normal basis on which an operator will judge the completeness of combustion, it is not an infallible guide. T. W. RICHARDS and H. S. DAVIS[8] determined the carbon monoxide in the residual gases and found, for benzene, that it was present only when unburnt carbon was visible; however, for toluene and decane, carbon monoxide was detected even when there was no residual carbon. Incidentally, of the various combustibles (mainly volatile) used by these workers, benzene, toluene, decane and benzoic acid were the materials most likely to give incomplete combustion. More refined methods for the determination of carbon monoxide are now available, the most convenient being the use of an infra-red (i.r.) spectrometer. With such an instrument (after

calibration in terms of carbon monoxide) it is possible to detect 10 or even 5 parts per million (p.p.m.)

It can be readily shown that the error in a determined heat release due to the presence of carbon monoxide in the residual gases (assumed to be at 25°C) is given by the following relationship; it is assumed that the effective heat capacity is not in error due to the presence of carbon monoxide in the residual gases in the standardization tests.

$$\text{Error} = 31{\cdot}77\ VPx \text{ cal} \qquad \ldots . [1]$$

where V = capacity of bomb (l.), P = final pressure in the bomb (atm absolute): it can be assumed to be equal to the initial pressure (P_i) when expressed in the same units, and x = carbon monoxide content of the residual gases in per cent by volume. For an error of 1 cal, with $V = \frac{1}{3}$ and $P = 31$ ($P_i = 30$ atm gauge), $x = 0{\cdot}0030$, which is equivalent to 30 p.p.m. Thus, for a heat release of 7500 cal, 30 p.p.m. of carbon monoxide would give an error of 0·013 per cent.

It appears that residual carbon monoxide is one of the chief reasons why a high standard deviation may obtain in a series of determinations of calorific value; since this source of error may arise without there being any visual indication of incomplete combustion, it seemed desirable to establish conditions which would, for different fuels, reduce the likely proportion of carbon monoxide to a very low value, preferably under 30 p.p.m.

COKE

Tests were made in which the residual gases from the combustion of a number of fuels under various conditions were fed to a calibrated i.r. spectrometer and the percentage of carbon monoxide read directly from the dial. The first series was made with some solid fuels of low reactivity: natural and artificial graphite, foundry and furnace coke, and 'Coalite'. The samples were burnt in the 1½ in. diameter nickel–chromium crucible (the 'coke crucible') on a layer of fine, granular alumina; they were fired by means of a length of cotton tied to the nickel–chromium wire through which the current passed, so that the crucible conditions were those recommended for coke in Part I[1]. The bomb was a Griffin–B.C.R.A. bomb of ⅓ l. capacity. Different initial pressures of oxygen were used, and the effect of adding a drop of water to the sample before firing was studied. Results are given in *Table 1.*

Table 1. Carbon monoxide (p.p.m.) in residual gases after combustion of unreactive fuels on alumina in 1½ in. diameter crucible at different initial pressures (P_i, atm gauge)

Material	*Dry sample*			*1 drop water added*		
	P_i=25	30	35	P_i=25	30	35
Natural graphite	170	50*	20	—	—	20
Electrode graphite	18*†	10*†	4*†,15	—	—	—
Foundry coke	>400	35*	68	175	44	20*
Furnace coke	350*†	45†	15	110	20	15
Coalite	—	—	—	—	—	5*

* Single tests; others means of at least two.
† 0·9 g; others 1·0 g.

These data show that, except in the case of the electrode graphite, there is a marked decrease in the concentration of carbon monoxide on increasing the initial pressure of oxygen from 25 to 30 atm and, usually, a further decrease on increasing the initial pressure to 35 atm. It was assumed that the combustion of carbon monoxide would be encouraged by the presence of hydroxyl, since most of the materials were of low moisture and hydrogen contents: hence the tests with one drop of water added to the sample before closure of the bomb. On the whole, the effect of this is favourable, though it may be that the extra precaution is only required for materials like the very unreactive foundry coke (Critical Air Blast 0·080, volatile matter 0·2 per cent).

COAL

The next series of tests was made on a high-volatile coal and an anthracite using the 1 in. diameter nickel–chromium crucible. The results are recorded in *Table 2.*

Table 2. Carbon monoxide (p.p.m.) in residual gases after combustion of coals in 1 in. diameter crucible at different initial pressures (P_i, atm gauge)

Material	*Volatile matter, % d.a.f.*	*Dry sample*			*1 drop water added*		
		P_i=25	30	35	P_i=25	30	35
Anthracite	6·6	>400*	80*	44	296*	52*	20
Coal	37·1	7*	10*	15*	—	—	—

* Single tests; others means of at least two.

The conventional use of an initial pressure of oxygen of 25 atm (gauge) for the high-volatile coal is shown to be satisfactory. The use of a higher initial pressure for anthracite is shown to be desirable, but even at 35 atm the proposed limit of 30 p.p.m. is exceeded with the dry sample, though the level is reduced by the addition of a drop of water. Further experiments are desirable to extend these observations, and the use of the 1½ in. diameter crucible should be studied.

LIQUID FUELS

A third series of tests was carried out using two crucibles for four liquid

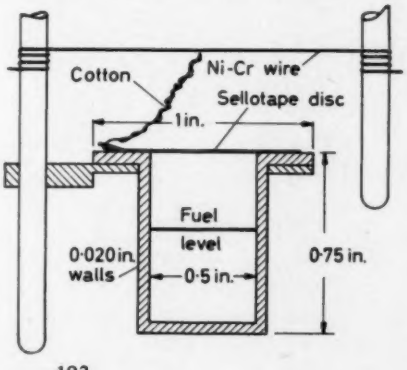

Figure 1. B.C.R.A. crucible for the combustion of iso*-pentane. Material:* Ni—Cr. *Other crucibles are used for other liquid fuels—see Tables 5 and 9*

fuels. Each crucible had a flange, by means of which it could be held in a ring fastened to the non-insulated pole of the bomb by means of a screw. The crucible, after the sample had been added, was closed with a disc of Sellotape, as shown in *Figure 1*. This method of sealing was completely effective, as shown by the data in *Table 3* for the loss of two of the most volatile fuels.

Table 3. Loss in weight of crucible plus sample; crucible of ½ in. top and bottom diameter, sealed with Sellotape

Time of standing (*min*)	*Loss in weight as percentage of weight* (*w*) *of sample*	
	Aviation spirit ($w = 0{\cdot}59$ g)	iso*Pentane* ($w = 0{\cdot}50$ g)
1	*Nil*	0·02
3	−0·06	0·02
5	−0·08	0·04
7	−0·11	0·06
9	−0·11	0·06
11	−0·10	0·10

The calorimeter tests were made using two nickel–chromium crucibles, each ¾ in. deep and of other dimensions as recorded, with the results in *Table 4*; each result is the mean from duplicate tests.

At all initial pressures used, petrol and aviation spirit give carbon monoxide contents below the suggested limit. For gas oil and benzene, the value of a high initial pressure in reducing the amount of residual carbon monoxide is

Table 4. Carbon monoxide (p.p.m.) in residual gases after combustion of liquid fuels in two crucibles at different initial pressures (P_i, atm gauge)

Material	*Crucible: ¾ in. top and bottom diameter*			*Crucible: ½ in. top, ¾ in. bottom diameter*		
	$P_i = 25$	30	35	$P_i = 25$	30	35
Benzene	100	60	48	—	—	—
Gas oil	100	73	14	68	33	25
Petrol	7	10	22	22	19	22
Aviation spirit	—	—	21	12	19	16

evident, but, even with $P_i = 35$ atm, the amount of carbon monoxide when burning benzene in the straight-sided (¾ in. diameter) crucible exceeds the limit. Benzene, like the solid fuels, gives a carbonaceous residue at the end of the flame period, and for such materials (excluding high-volatile coal and electrode graphite) the use of an initial pressure higher than 25 atm (gauge) seems desirable, though this is not sufficient to ensure 'complete combustion' (less than 30 p.p.m. of carbon monoxide) of benzene. This matter is considered again later in the paper.

THE B.C.R.A. WINDOW BOMB

One of the difficulties in establishing the correct conditions for calorimetry has been that the processes taking place inside the bomb have had to be assessed by external observations. It has long been recognized that actual visual observations of the combustion process would be very valuable, so it was decided to try to make a bomb with windows, as has been done by L. ZIEHL and W. A. ROTH[9].

Our first two models used Windonuts, designed for observation of the oil level in crank cases. In the first model, the Windonut was screwed into the top of the bomb, and in the second into an extension on the side. Both models suffered from the disadvantage that little could be seen of the contents of the bomb during the combustion period; this was due to both the small diameter (1 in.) and the inherent lack of clarity of the window. The design of the third model is shown in *Figure 2*. A 2 in. diameter window is used for viewing the

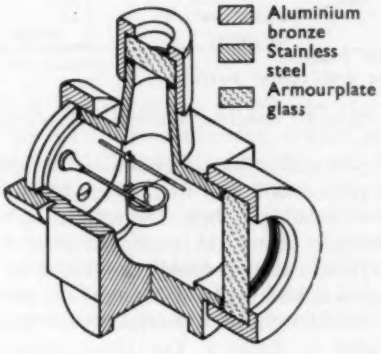

Figure 2. B.C.R.A. Window Bomb

elevation and a 1 in. diameter window for viewing the plan of the flame. The windows are made of toughened Armourplate glass, $\frac{1}{2}$ in. thick, and are secured by hand-tightening union nuts on rubber O-seals, as now used for securing the bomb cap in the Griffin–B.C.R.A. calorimeter bomb. In effect, this model, known as the B.C.R.A. Window Bomb, is a bomb on its side (but on a suitable stand) with an extension, on what is now the top, which carries the smaller window at a distance of about 4 in. above the base of the crucible. One end of the main cylindrical portion of the bomb carries the bomb 'cap', with the inlet/outlet valve and the terminals. The windows permit clear views of the interior of the bomb, and the use of prisms enables both views to be seen from one observation point.

Figure 3 shows drawings made from a ciné-film, taken through the 2 in. window, of the combustion of 1·2 g of briquetted benzoic acid in the special nickel–chromium foil crucible (Part III[3], Figure 2). It will be seen that the maximum flame height of about 2 in. is attained after about 10 sec; subsequently, the pellet swells though the flame becomes shorter. The flame expires after about 45 sec, leaving a glow which is extinguished in 60 to 68 sec. The glow is probably due to the burning of residual carbon.

Visual observations have been made for a variety of materials, using different crucibles. For light liquid paraffin hydrocarbons the total combustion period is very little longer than the actual flame period. On the other hand, heavier paraffin hydrocarbons—such as gas oil—give a longer period between extinction of the flame and the end of the combustion. Benzene, tar, pitch and

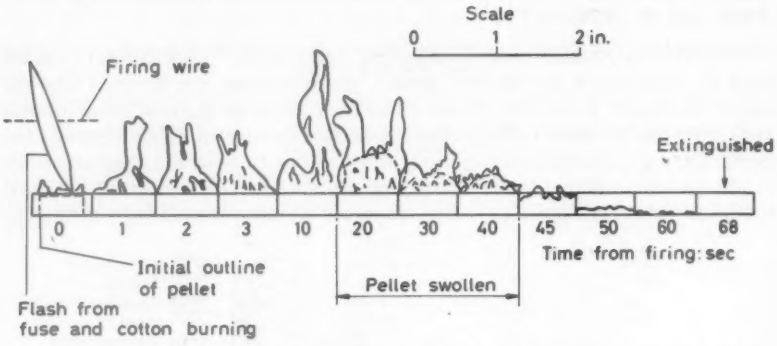
Scale
0 1 2 in.
Firing wire
Extinguished
0 1 2 3 10 20 30 40 45 50 60 68
Time from firing: sec
Initial outline of pellet
Pellet swollen
Flash from fuse and cotton burning

Figure 3. Combustion of benzoic acid as observed in the B.C.R.A. Window Bomb

coal give still longer intermediate periods, increasing in that order, whilst coke gives only a very small flame which it is difficult to distinguish from the glow of burning carbon. The lengths of both the flame and glow periods are modified by changes in the top diameter of the crucible and the initial pressure of oxygen. *Table 7* records the results of a series of tests in which the heat release was always about 7500 cal but in which the initial pressure was varied and in which various crucibles were used. The details of the crucibles are recorded in *Table 5.* The characteristics of the materials (including the aviation spirit used in other tests) are recorded in *Table 6.* Benzoic acid was briquetted before combustion. Benzene, petrol and *iso*pentane were burnt according to the method already described in this paper. Gas oil was burnt in an 'open' crucible (one not sealed with Sellotape). Crucible No. 1 is the special foil crucible for benzoic acid; No. 2 (included in *Table 5* for completeness) is the coke crucible; No. 3 is the coal crucible. In the tests recorded in

Table 5. Details of crucibles

Crucible No.	1	2	3	4	5	6	7	8
Diameter (in.)								
Top	0·6	1·5	1·0	0·75	0·75	0·5	0·5	0·25
Bottom	0·6	1·5	1·0	1·0	0·75	0·75	0·5	0·25
Height (in.)	0·25	0·75	0·75	0·75	0·75	0·75	0·75	1·0
Capacity (ml)	1·4	12·4	7·6	6·4	5·5	3·5	2·5	2·2
*Wall thickness** *(in.)*	0·01	0·05	0·02	0·02	0·02	0·02	0·02	0·01
Weight (g)								
Ni-Cr	1·4	39·8	16·2	16·1	7·0	7·7	9·2	10·2
Silica	—	15·6	11·7	13·1	—	—	9·9	—

* Of nickel–chromium version; wall thickness of silica crucibles: 1 to 2 mm.

Table 7, only nickel–chromium crucibles were used, but *Table 5* shows that silica equivalents of a number of the crucibles were available. A considerable number of tests were made using the silica crucibles, but it was concluded that the silica version was never as satisfactory as the equivalent nickel–chromium crucible, the combustion period usually being excessively long and the tendency for unburnt carbon to remain being greater.

Table 6. Characteristics of fuels

Fuel	*Melting point (°C)*	*Boiling point (°C)*		*Specific gravity*
		Initial	*Final*	
iso*Pentane*	—	28	28	0·62
Aviation spirit	—	35	115	0·72
Petrol	—	41	135	0·73
Benzene	—	80	80	0·88
Gas oil	—	180	>350	0·87
Benzoic acid	122	—	—	1·32*

* Apparent specific gravity: as received, 0·17; as used (pelleted), 1·14.

The essential requirement which it was sought to satisfy was that, for each fuel, the crucible and pressure finally recommended should ensure complete combustion with values of T_f and T_c approximately the same as for benzoic acid. As mentioned in the introduction to this paper, the initial approach was an attempt to modify the characteristics of benzoic acid to conform with those of a variety of fuels. For liquid fuels, this required the combustion of benzoic acid to be accelerated, which can be achieved by using loose (non-briquetted) benzoic acid or benzoic acid which has been briquetted and then broken. Tests were made under such conditions using

Table 7. Burning characteristics of various fuels in B.C.R.A. Window Bomb; heat release 7 500 cal; nickel–chromium crucibles

Fuel	P_i *(atm, gauge)*	*Crucible Nos.*													
		1		3		4		5		6		7		8	
		T_f	T_c	T_f	T_c	T_f	T_c	T_f	T_c	T_f	T_c	T_f	T_c	T_f	T_c
Benzoic acid	25	45	68	—	—	—	—	25	45	42	68	—	—	—	—
	30	37	54	—	—	—	—	25	32	45	67	—	—	—	—
	35	40	48	—	—	—	—	23	30	34	56	—	—	—	—
Benzene	25	—	—	14	32	18*	45*	20	50	38	148†	110	177	—	—
	30	—	—	—	—	17	31	20	38	39	124	—	—	—	—
	35	—	—	—	—	13*	20*	20	34	37	93	—	—	—	—
	40	—	—	—	—	—	—	—	—	45	76	—	—	—	—
Gas oil	25	—	—	20*	27*	20*	36*	36	53†	—	—	—	—	—	—
	30	—	—	—	—	—	—	28	44†	48	69	—	—	—	—
	35	—	—	—	—	—	—	25	35	38	51	—	—	—	—
Petrol	25	—	—	11	13†	16	19	22	25†	138	158†	—	—	—	—
	30	—	—	—	—	—	—	19	20	62	69†	66	110	—	—
	35	—	—	—	—	—	—	15	18	34	39	58	74	—	—
iso*Pentane*	25	—	—	—	—	—	—	—	—	—	—	22	22	87	91
	30	—	—	—	—	—	—	—	—	—	—	20	20	40	50
	35	—	—	—	—	—	—	—	—	—	—	—	—	34	34

T_f = flame period (sec). T_c = total combustion period (sec).
* denotes single tests; others means of at least two.
† denotes residue of unburnt carbon in crucible.

crucibles Nos. 1 and 6, and a platinum crucible of top diameter 1 in., bottom diameter 0·8 in. and height 1 in. However, these tests confirmed the conclusion drawn in Part III[3], that briquetting is essential: if burnt in either of the less compact conditions, there is invariably a residue of unburnt carbon and a significantly large amount of carbon monoxide in the gases.

If the standard conditions for the combustion of benzoic acid be taken as the use of crucible No. 1 and $P_i = 25$ atm, as seems feasible (and it was found that the proportion of carbon monoxide in the residual gases under these conditions did not exceed 10 p.p.m.), T_f and T_c under the conditions chosen for any particular fuel should, ideally, be in reasonable agreement with the appropriate values for benzoic acid, namely, 45 and 68 sec, respectively. On this basis, conclusions were drawn as to suitable conditions for various fuels, but these conclusions could only be regarded as tentative, owing to the different shape and greater mass of the B.C.R.A. Window Bomb as compared with a normal calorimeter bomb. These differences lead to slower combustion in the Window Bomb under otherwise identical conditions, as indicated by higher values of T_m, the time for 60 per cent of the temperature rise of the water to occur. The final confirmation was therefore sought under the conditions of normal bomb-calorimetric determinations.

TESTS IN THE GRIFFIN–B.C.R.A. ISOTHERMAL CALORIMETER

The Griffin–B.C.R.A. Isothermal Calorimeter (see Part VIII[5]), used in conjunction with a platinum resistance thermometer and a Smith's Difference Bridge, was employed in the final series of tests on liquid fuels. *Table 8* records the mean results, and the standard deviations, for groups of (usually) six determinations under various conditions on three of the four liquid fuels

Table 8. Results of tests on four liquid fuels in Griffin–B.C.R.A. Isothermal Calorimeter

Fuel	P_i (*atm, gauge*)	*Crucible No.* 5			6			7			8		
		$\overline{T_m}$	$\bar{n}$	σ	$\overline{T_m}$	$\bar{n}$	σ	$\overline{T_m}$	$\bar{n}$	σ	$\overline{T_m}$	$\bar{n}$	σ
Benzene	25	—	—	—	84	8·8	0·09	—	—	—	—	—	—
	30	—	—	—	69	8·5	0·03	—	—	—	—	—	—
	35	—	—	—	62	9·2	0·24	—	—	—	—	—	—
Gas oil	25	61	8·0	0·19	83	8·5	0·14	—	—	—	—	—	—
	30	60	8·5	0·15	76	9·0	—*	—	—	—	—	—	—
	35	60	8·0	0·07	78	8·3	0·06	—	—	—	—	—	—
Aviation spirit	25	—	—	—	65	8·9	0·12	67	8·9	0·12	—	—	—
	30	—	—	—	62	8·3	—*	70	8·7	0·18	—	—	—
	35	—	—	—	59	8·3	0·07	—	—	—	—	—	—
iso*Pentane*	30	—	—	—	—	—	—	—	—	—	134	10·7	0·22
	35	—	—	—	—	—	—	57	7·7	0·08	120	10·2	0·14
	40	—	—	—	—	—	—	—	—	—	113	10·0	0·31

P_i = initial pressure of oxygen.
$\overline{T_m}$ = mean time to 60 per cent of total temperature rise (sec).
$\bar{n}$ = mean length of chief period, as assessed by the rule of Part III[3] (min).
σ = standard deviation (per cent of mean calorific value).
* = two tests only; six in each other group.

of *Table 7* and on a sample of aviation spirit. The conditions (crucible and initial pressure) included those which were considered likely to prove satisfactory.

For agreement with the combustion characteristics of benzoic acid (in crucible No. 1 at $P_i = 25$ atm, gauge), it is considered sufficient for $\overline{T_m}$ to be within the range of 63 $\pm$ 6 sec and for $\bar{n}$ to be within range 8·0 $\pm$ 0·5 min. *Table 9* gives, for each of the four fuels, the conditions now recommended on this basis.

Table 9. Results of six tests on each of four liquid fuels under recommended conditions in Griffin–B.C.R.A. Isothermal Calorimeter

Fuel	*Crucible No.*	P_i *(atm, gauge)*	$\overline{T_m}$ *(sec)*	$\bar{n}$ *(min)*	σ *(per cent)*
Benzene	6	30	69	8·5	0·03
Gas oil	5	35	60	8·0	0·07
Aviation spirit	6	35	59	8·3	0·07
iso*Pentane*	7	35	57	7·7	0·08

It will be seen that, under the chosen conditions, not only are the combustion criteria fulfilled but the standard deviation is always satisfactorily low.

Apart from the accurate specification of the various crucibles which it is desirable to use, the outstanding conclusions from this work on liquid fuels is the recommendation of an initial pressure of 35 atm (gauge) for all paraffin hydrocarbons. Under the conditions used in the tests reported in Part II[2], this did not appear to be necessary; the tests reported here have shown that it is necessary for two reasons: to reduce the carbon monoxide content of the residual gases to negligible proportions (*Table 4*) and to secure identity of thermal conditions with those obtaining in the standardization of the calorimeter. It should be remembered that calorific values vary with the pressure, so that, strictly, it is necessary to make allowance when comparing fuels for which different pressures have been used; in practice, however, the difference is often negligible.

THE CALORIFIC VALUE OF *ISO*PENTANE

It is convenient to record here the work in which the method of treatment of liquid fuels used throughout the tests reported in this paper was developed. This work was concerned with the determination of the calorific value of *iso*pentane, which was previously discussed in Part II[2]. The authors of that paper (J. E. Barker and R. A. Mott) reported a value of 11702 cal_{15}/g. R. L. Le Tourneau and R. Matteson[10] gave a value of 20884 B.t.u./lb; assuming their heat unit to be the I.T.B.t.u. (1 I.T. cal = 4·1867 J), their value is equivalent to 11606 cal_{15}/g. The American Petroleum Institute[11] give the heat of combustion at constant pressure as 11606 cal/g, the calorie being defined as 4·1840 J; converting to constant volume, this value is equivalent to 11577 cal_{15}/g.

To try to explain the discrepancy between the Barker–Mott value and the two others (which are in reasonable agreement), tests were made according to the procedures recommended by Barker and Mott and by Le Tourneau and Matteson. It was found impossible to achieve complete combustion by either method: the Barker–Mott technique gave unburnt material on the bomb walls and the Le Tourneau–Matteson technique gave heavy smears of soot in the crucible and occasionally on the walls. The use of alumina in the Le Tourneau–Matteson crucible did not improve the performance, and it may be of interest to note that complete combustion of 'very volatile gasoline' could not be obtained by the Le Tourneau–Matteson method. The tests reported by Barker and Mott were all carried out in a Sutton bomb: the failure of the method when using a B.C.R.A. bomb (C design: Part V[6], Figure 8: 0·33 l. capacity) may be due to the difference in the dimensions of these bombs. (It should be pointed out that, even in the B.C.R.A. Bomb C, the Barker–Mott method is satisfactory, in terms of visibly complete combustion, for gas oil, benzene and aviation spirit.)

It seemed likely that the Le Tourneau–Matteson method could be improved by a reduction in the mass of the crucible. Consequently, a new crucible was made according to the general design of Le Tourneau and Matteson but with the thickness of the walls and base reduced to 0·010 in. and the thickness of the flange reduced to 0·050 in. It was found that, using this crucible (No. 8), only small smears of soot remained (in the crucible) after combustion. This crucible, and the Le Tourneau–Matteson technique, were then used in three series, each of six determinations, at 30, 35 and 40 atm (gauge) initial pressure of oxygen. After each test, the weight of unburnt carbon in the crucible was found by burning-off and a correction applied to the observed calorific value, taking the calorific value of carbon as 7900 cal/g. The results (also used in *Table 8*) are summarized in *Table 10*.

Table 10. Determination of calorific value of iso*pentane using modified Le Tourneau–Matteson method*

P_i (*atm, gauge*)	$\overline{T_m}$ (*sec*)	$\bar{n}$ (*min*)	*Mean correction* (*cal/g*)	*Mean corrected calorific value* (cal_{15}/g)	σ (*per cent*)
30	134	10·7	8	11571	0·22
35	120	10·2	5	11607	0·14
40	113	10·0	4	11593	0·20

These data accorded with the Le Tourneau–Matteson and American Petroleum Institute values and showed that the thermal effect of the smears was small. However, as a residue of solid carbon might imply the presence of carbon monoxide in the gaseous phase at the end of combustion, no value derived from tests in which smears occurred could be accepted as being reliable. (The Barker–Mott value was derived from seven tests in which combustion appeared to be complete.) A crucible was then designed which, used with the Le Tourneau–Matteson firing technique, gave a better than 50 per cent chance of complete combustion (as judged by the absence of smears in the crucible after the combustion) in tests on *iso*pentane. This was

a crucible conforming to the dimensions of No. 7 of *Table 5*, except that the wall thickness was only 0·010 in. The method of use was as illustrated in *Figure 1*.

In a series of eight tests using an initial oxygen pressure of 35 atm (gauge), combustion appeared to be complete in six tests, the results of which have been summarized in *Tables 8* and *9*. The mean calorific value obtained from these tests was 11 707 cal_{15}/g and the standard deviation was 0·08 per cent of this mean. Thus the result is in good agreement with the Barker–Mott value, and the observed repeatability is very good. (The standard deviation in the series reported by Barker and Mott is 0·15 per cent of the mean value. The average deviation of the 3 results quoted by Le Tourneau and Matteson is 0·14 per cent of the mean value.) It seems that the Le Tourneau–Matteson and American Petroleum Institute values are low by 100 to 125 cal/g, presumably due to incomplete combustion in their determinations. The condition for a reasonable chance of complete combustion being attained seems to be that T_m (time to 60 per cent of the total temperature rise) should be about 60 sec; the Barker–Mott method (giving T_m *ca.* 35 sec) permits too rapid combustion (at least in the B.C.R.A. Bomb C) and the Le Tourneau–Matteson method gives too slow combustion, even with the modified (lower mass) crucible.

It may be noted that, as indicated in *Table 9*, a crucible conforming exactly to the details of No. 7 (*Table 5*) is now considered to be satisfactory; the wall thickness need not be less than 0·20 in., which makes for easier fabrication and a longer life.

RECOMMENDED CONDITIONS FOR SOLID FUELS

All bituminous coals which we have tested give visibly complete combustion when burnt in crucible No. 3 with $P_i = 25$ atm (gauge), and the combustion characteristics are substantially the same as for benzoic acid in crucible No. 1 and the same value of P_i. The one coal which we have used when determining carbon monoxide in the residual gases gave a negligible amount (*Table 2*); further tests are, of course, desirable.

For anthracites, also using crucible No. 3, it is necessary to raise P_i to 35 atm gauge, and desirable also to add a drop of water to ensure 'complete' combustion; at this higher pressure the combustion characteristics do not differ materially from those obtaining when burning benzoic acid under the conditions defined above. This may also apply to some low-volatile coals.

Like anthracite, coke (crucible No. 2) must be burned with $P_i = 35$ atm (gauge), and preferably with a drop of water added. Under these conditions combustion is 'complete', but the characteristics differ from the standard in that the period of combustion is significantly longer than that of benzoic acid. This difficulty has been overcome by evaluating the minimum length of chief period necessary to ensure a negligible effect of the burning characteristics on the subsequent variations of the effective heat capacity for the combustion of both benzoic acid and coke. Data given in Part VII[4] suggested that this might be of the order of 15 min, but it has been found that 10 min is adequate in the Griffin–B.C.R.A. Isothermal Calorimeter.

It was necessary to establish the form of the variation of the effective heat capacity for lengths of chief period of up to 20 min. This was done, in six tests with benzoic acid, by continuing temperature observations for 25 min after firing. A similar series of tests was then carried out with a number of cokes. For each coke, the form of the variation of the mean corrected temperature rise was compared with the form of the variation of the mean effective heat capacity. It was considered likely that, for any coke, the form would be found to be similar to that for benzoic acid after the lapse of a certain period (sufficient for the effect of temperature lags to have been eliminated). The minimum period necessary to ensure this for all the cokes tested was 10 min, and this is the correct value to apply in the calibration of the calorimeter for use with coke and in all determinations of the calorific value of coke.

As shown in Part VIII[5], the repeatability of effective heat capacity when burning benzoic acid in the Griffin–B.C.R.A. Isothermal Calorimeter varies little for lengths of chief period from 7 to 10 min. As 10 min is now known to be the acceptable minimum when standardizing the calorimeter for tests on coke, it is suggested that this value be adopted for all determinations made with this calorimeter, provided that it is used at all for coke. If it is not to be used for coke, the choice can still be made purely on a basis of repeatability in the standardization.

CONCLUSIONS

Data given in Table 4 of Part VIII[5] of this series show that the observed effective heat capacity of a bomb calorimeter may vary by as much as 1·9 cal/°C according to the point selected as the end of the chief period, even given compliance with the rule suggested in Part III[3] and now accepted in the British Standard[12]. Such variation is equivalent to a variation of approximately 6 cal/g in a determined calorific value.

Data given in this paper show that the absence of unburnt carbon at the end of the determination does not necessarily mean that combustion has been complete. In fact, it seems likely that there is always a certain amount of carbon monoxide in the gaseous phase.

Methods of overcoming these sources of error have been considered. The possibility of error due to variation of effective heat capacity can be eliminated; the possible error due to the presence of carbon monoxide in the gaseous phase can be reduced to negligible proportions. The steps necessary to achieve these objectives are summarized below.

(*1*) The conditions for the combustion of samples of various materials shall be as follows (for details of crucibles, see *Table 5*).

(*a*) Benzoic acid: briquetted; crucible No. 1; $P_i = 25$ atm (gauge).

(*b*) Coal: loose; crucible No. 3; $P_i = 25$ atm (gauge).

(*c*) Anthracite (and possibly low-volatile coal); loose; crucible No. 3; one drop* of water added; $P_i = 35$ atm (gauge).

* To avoid incomplete combustion in the solid phase, the quantity of water must not exceed 0·05 ml (see part IX[13]); this amount is best added from a semi-microburette.

(*d*) Coke: loose; on 0·75 g alumina; crucible No. 2; one drop* of water added; P_i = 35 atm (gauge).

(*e*) Benzene: method of *Figure 1*; crucible No. 6; P_i = 30 atm (gauge).

(*f*) Gas oil: method of *Figure 1*, except that the crucible need not be sealed with Sellotape; crucible No. 5; P_i = 35 atm (gauge).

(*g*) Aviation spirit: method of *Figure 1*; crucible No. 6; P_i = 35 atm (gauge).

(*h*) *iso*Pentane: method of *Figure 1*; crucible No. 7; P_i = 35 atm (gauge).

(*2*) The length of chief period shall then be the same in all determinations (in a given calorimeter), whether of effective heat capacity or of calorific value, and irrespective of the particular fuel being studied. If coke is not to be tested, the length shall be that giving the best repeatability in determinations of effective heat capacity (7 min in the Griffin–B.C.R.A. Isothermal Calorimeter). If coke is to be tested, a greater length will be necessary: the value has been assessed at 10 min for the Griffin–B.C.R.A. Isothermal Calorimeter.

(*3*) Provided that the recommended combustion conditions are applied, the use of a constant length of chief period is now considered to be better practice than the application of the rule recommended in Part III[3] and accepted in the British Standard[12].

(*4*) With a bomb of $\frac{1}{3}$ l. capacity, the effective heat capacity of the system (determined with P_i = 25 atm, gauge) is increased by 0·5 and 1·1 cal/°C when using P_i = 30 and 35 atm (gauge), respectively.

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* To avoid incomplete combustion in the solid phase, the quantity of water must not exceed 0·05 ml (see Part IX[13]); this amount is best added from a semi-microburette.

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Microscopic Studies of Rate of Thermal Decomposition of Petrographic Components of Coal

S. ERGUN, H. J. O'DONNELL and B. C. PARKS

Studies were made of the thermal behaviour of the petrographic components of coals by determining times required for fusion and resolidification at constant temperatures in the range 450° to 500°C. Data collected on exinites permitted a systematic kinetic analysis. The temperature coefficients of time lapse before fusion for two exinites, one containing 7·6 per cent hydrogen, the other 6·5 per cent, were 86 and 61 kcal/mole, respectively. However, the temperature coefficients of total reaction times were about the same, 44 kcal/mole and 50 kcal/mole, respectively. Vitrinites from two high volatile bituminous coals were studied in a narrower temperature range, 464° to 490°C. Reproducibility of data was poor. The temperature coefficient of time lapse before fusion was estimated to be about 100 kcal/mole. Reactions of micrinite and fusinite components could not be studied quantitatively under the microscope. Qualitative observations showed that exinites and vitrinites heated at slow rates behaved differently from those heated instantaneously, as in the present study. Under the former conditions, high temperature coefficients of time required for fusion, especially of vitrinites, suggested that depolymerization or cracking is the initial step of thermal decomposition.

QUALITATIVE microscopic studies of the effect of heat on coal and coal components have been reported by several investigators[1–4]. In the course of some preliminary quantitative thermal studies of the petrographic components of a high volatile bituminous coal, it was observed that exinite (in microscopic quantities) fused and resolidified over a wide temperature range, the duration of reaction becoming shorter with increase in temperature. Vitrinite and, to a smaller degree, micrinite fused only at relatively high temperatures, that is, when they decomposed rapidly. Fusinite showed no visible change at any temperature. The temperature coefficients of the thermal decomposition of exinites and vitrinites were studied by using a microscope fitted with a heating stage.

APPARATUS AND EXPERIMENTAL PROCEDURE

The heating stage was a commercial unit designed for use with microscopes having vertically adjustable circular object stages. It contained a hollow ceramic core with grooves on its interior surface to hold the resistance wire in place. A metal tube was fitted inside the ceramic core to distribute heat more uniformly and to permit vertical upward illumination for examination of thin sections in transmitted light. At the top, the tube was provided with a collar that served as a seat for circular quartz discs on which the samples rested. Thermocouple wires were introduced through a hole in the side of the seat to measure the temperature of the disc. The coil assembly was enclosed inside a cylindrical, double-walled metal chamber that was cooled with circulating water. At its base the chamber had a quartz window opposite

the metal tube. At the top it had an eccentric revolving cover with three quartz windows and an open window. When the cover was rotated into position, one of its windows faced the sample disc. The chamber was airtight and provided with inlet and outlet tubes for circulating inert gas.

The heating stage was modified to include a second thermocouple for maintaining constant temperature, which was accomplished by means of a phototube relay system actuated by a galvanometer. Also, a side tube was inserted near the top of the chamber to introduce a removable microspoon assembly that permitted instantaneous dropping of samples on to the quartz disc. Before the sample was dropped, the microspoon could be held back near the water-cooled wall of the chamber; a push and a twist, both movements being guided, placed the sample on the disc. The temperature of the disc, as measured by the Pt/Pt–Rh thermocouple, was calibrated by determining melting points of seven pure metals and compounds in a range from 122° to 790°C. The observed temperatures agreed with the melting points within 2°C.

Concentrates of the four major petrographic components of a high volatile bituminous coal and of three additional exinites and one vitrinite were studied. The concentrates were obtained by centrifugal separation in salt solutions of adjusted specific gravity[5]. The petrographic and chemical analyses of the concentrates are shown in *Tables 1* and *2*. Only two exinites and one

Table 1. Petrographic analysis of component concentrates by reflected light method

Concentrates	*Observed contents of components, per cent*			
	Vitrinite	*Exinite*	*Micrinite*	*Fusinite*
Hernshaw vitrinite	94	3	2	1
Hernshaw exinite	0	86	14	0
Hernshaw micrinite	1	11	87	1
Hernshaw fusinite	4	0	0	96
Pittsburgh vitrinite	100	0	0	0
Michigan exinite	0	98	2	0
*Wilhelm exinite**	0	97	3	0
Pocahontas exinite†		?		

* Analysis taken from published data[6].
† The concentrate was obtained from a cannel layer of medium volatile Pocahontas coal. The reflectances of this exinite concentrate and those obtained from higher rank coals were about the same as those of the associated vitrinites; therefore, a petrographic analysis of the pulverized (minus 325-mesh) concentrate could not be made.

Table 2. Chemical composition of coal components

Concentrates	*Volatile matter, per cent*	*Ultimate analysis, moisture- and ash-free basis, per cent*				
		H	C	N	O	S
Hernshaw vitrinite	33·7	5·4	85·2	1·6	7·2	0·6
Hernshaw exinite	55·3	6·5	86·2	1·1	5·5	0·7
Hernshaw micrinite	31·4	4·8	85·9	0·7	8·0	0·6
Hernshaw fusinite	13·4	3·2	91·5	0·6	4·3	0·4
Pittsburgh vitrinite	36·0	5·3	84·1	1·6	8·0	1·0
Michigan exinite	77·0	7·6	80·6	1·0	9·4	1·4
*Wilhelm exinite**	22·6	4·9	89·3	1·4	3·8	0·6
Pocahontas coal†	24·3	5·1	89·6	1·3	3·3	0·7

* Analysis taken from published data[6].
† A separate analysis of the exinite concentrate was not made.

vitrinite could be studied extensively. The particle sizes utilized were 150- to 200- and 325- to 400-mesh for the Michigan exinite and 325- to 400-mesh for the others.

When a sample (about 0·2 mg) was dropped with the microspoon on to the quartz disc, no change was observed for a number of seconds. Then the sample began to fuse, starting with the particles in contact with the disc. The fusion spread rapidly, and the particles formed a big globule. At this stage devolatilization was rapid, as manifested by the formation of gas bubbles bursting out of the globule. Eventually bubbling ceased, leaving behind a flattened residue that solidified quickly. Except for a slight darkening, no change in appearance of the residue was seen by further observation. The cessation of bubbling to yield a quickly solidifying residue was more or less abrupt for exinites.

Microscopic observations were made with reflected light, using 97·5× magnification. Constant temperatures ranging from 448° to 503°C were used in most of the experiments at 1°C intervals. At each temperature a minimum of 10 observations was made, about 0·2 mg sample being introduced with the microspoon each time. Time lapse before fusion and the duration of reaction were measured with a stopwatch, the latter corresponded to time elapsed between dropping the sample on the disc and resolidification of the fused fragment. Reaction durations less than seven seconds were not considered on account of the possible errors involved in recording. In general, when no fusion was visible in about two minutes, the sample charred without an appreciable change in appearance.

DISCUSSION OF RESULTS

The reproducibility of the quantitative measurements described above was poor; therefore, experiments at each temperature were repeated nine times or more. The r.m.s. error in repeated experiments with exinites was ±27 per

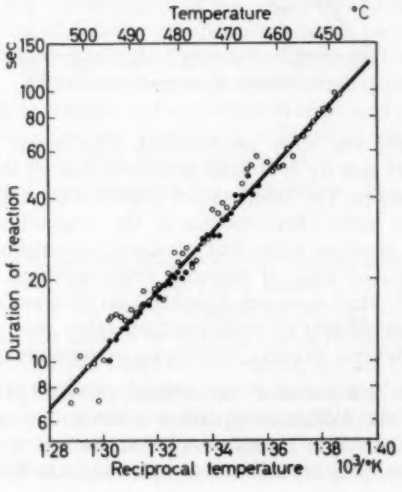

Figure 1. Temperature dependence of the fusion and resolidification of exinites. ○ Hernshaw exinite, ● Michigan exinite

cent. The average results of total reaction time measurements for two exinites are represented graphically in *Figure 1* as a function of reciprocal temperature, that is, an inverse Arrhenius plot. From inspection of the figure, the temperature coefficients of both exinites appeared to be the same. When separate least squares lines were calculated, the slope of the line for the Hernshaw exinite was found to correspond to an activation energy of 50 $\pm$ 1 kcal/mole and that for the Michigan exinite to 44 $\pm$ 1 kcal/mole. A least squares line common to both exinites (the line shown in *Figure 1*) yielded 49 $\pm$ 1 kcal/mole. The r.m.s. errors indicated were calculated from deviations of the observed average values from those calculated by least squares, that is, from the residual errors.

A similar plot of the average values for time lapse before fusion is shown in *Figure 2*. In this respect, the difference in the thermal behaviour of the two

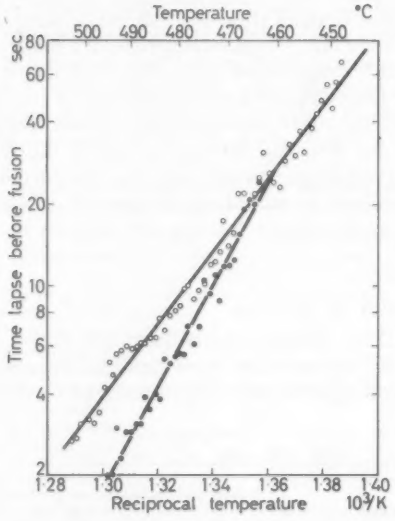

Figure 2. Temperature dependence of time lapse before fusion. ○ Hernshaw exinite, ● Michigan exinite

exinites was more pronounced. The energy of activation of the Hernshaw exinite was 61 $\pm$ 1 kcal/mole and that of the Michigan exinite was 86 $\pm$ 1 kcal/mole. The temperature dependence of time lapse before fusion appears to be more characteristic of the original sample than the dependence of total reaction time. The observed activation energy is high, suggesting that the initial step of thermal decomposition involves breakage of primary bonds, that is, a depolymerization or cracking process. The lower temperature coefficient of total reaction times may signify simultaneous occurrence of a reverse process, reforming or repolymerization.

The low value of the variance (about 2 per cent) of average reaction times from the Arrhenius equation is interesting especially in view of the fact that r.m.s. error in repeated experiments was $\pm$27 per cent. The latter signifies that exinites are macroheterogeneous; the heterogeneity could be with respect

to size and/or composition of polymers that constitute exinites. The low variance from the Arrhenius equation indicates that energy of activation required for depolymerization (cracking) is, more or less, independent of the size of polymers.

Vitrinites and high rank exinites, for example, Pocahontas and Wilhelm, appeared to fuse at somewhat higher temperatures and reproducibility of data was poor. The Hernshaw and Pittsburgh vitrinites fused at temperatures above 460°C. At 500°C the reaction was too rapid to follow. The resolidification of the fused vitrinites was not abrupt as in the case of low rank exinites; therefore, measurements were confined to time lapse before fusion. The r.m.s. error in repeated experiments was as large as 60 per cent. A statistical analysis of data collected in the temperature range of 464° to 490°C yielded an energy of activation in excess of 100 kcal/mole. This is definitely indicative of the breakage of primary bonds.

The results reported above are not by themselves sufficient to support conclusions regarding the mechanism of thermal degradation of coals, yet they are novel and throw light on some interesting aspects of thermal degradation. Coal components are poor heat conductors; when an appreciable quantity of coal, for example one gramme or more, is used in kinetic experiments, it is very difficult to heat the sample to elevated temperatures in a few seconds and study its isothermal behaviour. Therefore, previous workers, e.g. D. FITZGERALD[7–8] and H. A. G. CHERMIN and D. W. VAN KREVELEN[9], devised heating programmes in studying rates of weight loss, evolution of various gases, changes in viscosity, and other factors and were able to conduct such studies over a wide range of temperatures. For example, Fitzgerald[8] studied the pyrolysis of an exinite in the temperature range 350° to 700°C by raising the temperature of a 3g sample at a rate of 1·8°C per minute. In *Figure 1* of this report, it is seen that, in the temperature range 450° to 500°C, observed reaction times ranged from 100 to about 7 seconds. When a sample of Hernshaw exinite was dropped on the quartz disc at 450°C and the temperature raised at a rate of 2°C per minute, the reaction observed under the microscope was complete in less than 2 minutes, that is, before the temperature was raised by 4°C. Therefore, it is seen that temperature coefficients (energies of activation) calculated in the present studies and those reported by Fitzgerald and Chermin and van Krevelen should not necessarily be compared. This can also be inferred from the excessive difference in relative rates of reaction; in terms of time required for completion, the rates reported here are high.

The effect of rate of heating on the thermal behaviour of vitrinites and exinites was also investigated in a more or less qualitative manner. A sample (about 0·2 mg), when heated from 300° to 550°C at a rate of 2°C per minute, showed no sign of fusion. To fuse the sample by heating it at a programmed rate, it was found necessary to raise the temperature rapidly to the fusion level. These experiments show that heating history has a pronounced effect on the thermal behaviour of a residue. It follows that, when pyrolysis of coal components is studied by a programmed rate of heating, the information obtained at any temperature relates to the residue at that stage, and the

temperature coefficients computed from such information depend largely on the process. In this respect, the temperature coefficients obtained in the present study are better defined; that is, they relate to the original sample.

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Studies on Oxidation of Coal at Lower Temperatures

J. N. BHOWMIK, P. N. MUKHERJEE and A. LAHIRI

The mechanism of aerial oxidation of coal (at 200°C) is discussed with reference to the intermediate steps of the reaction. From an estimation of the oxygen-containing functional groups in oxidized coal as well as hydrolysed samples, it is shown that there is a stoichiometric relation between the —COOH and phenolic —OH groups that are formed on hydrolysis. Also, the increase in these acid groups is shown to be accompanied by the decline in the =CO groups. On the basis of the above observations, the various probable mechanisms of the reaction are discussed.

MUCH work has been done on the oxidation of coal[1] under various conditions, and different oxidizing agents have been employed. The present work was primarily concerned with the study of the aerial oxidation of coal at 200°C with a view to interpreting the mechanism of the process. Recently papers[2,3] have appeared on the subject and a fair picture of the changes that are brought about during the course of oxidation of coal in a stream of air is now available. The broad pattern of changes that has emerged from these studies may be summed up as follows.

Coals react with atmospheric oxygen to form —COOH, —OH and =CO groups and the exact percentage of oxygen in the form of these functional groups depends on the rank of the coal as well as the temperature and duration of the oxidation.

The investigations presented here were undertaken to find out the intermediate steps in the reaction between coal and air at 200°C. A sample of coal was oxidized in a restricted supply of air in an air oven maintained at 200°C and the products were withdrawn at different stages and their properties examined.

The oxidized coal samples were examined for the distribution of functional groups such as —COOH, —OH and =CO by the methods discussed below. Also, the samples were hydrolysed in alkaline medium and the groups estimated to ascertain if some parts of the functional groups are present in the form of esters or in similar combinations. From the elemental composition, density, and functional group estimation, the ring index and aromaticity of the oxidized samples were calculated by D. W. VAN KREVELEN and H. A. G. CHERMIN's[4] method.

EXPERIMENTAL

A sample of low rank coal (analysis, *Table 1*) was oxidized in an air oven at a temperature of 200°C for a period of 300 h and samples were withdrawn at 100, 200 and 300 h. The supply of air to this oven was adjusted to allow the oxidation reaction to proceed very slowly.

A part of the original sample as well as each of the oxidized samples was hydrolysed by treatment with alcoholic caustic potash solution.

Hydrolysis

About 10 g of the sample was treated with 250 cm³ of 5N alcoholic caustic potash solution and refluxed for 3 h. The refluxed sample was then acidified

Table 1. Elemental analysis of the samples (d.a.f. basis)

Coal sample	C%	H%	N%	'O + S' %
Jambad	79·4	5·2	1·9	13·5
Jambad (hydrolysed)	79·6	5·2	1·9	13·3
Oxidized Jambad (100 h, 200°C)	71·4	3·6	1·8	23·2
Oxidized Jambad (100 h, 200°C) hydrolysed	70·4	3·8	1·8	24·0
Oxidized Jambad (200 h, 200°C)	70·4	3·3	1·8	24·5
Oxidized Jambad (200 h, 200°C) hydrolysed	69·3	3·4	1·9	25·4
Oxidized Jambad (300 h, 200°C)	68·9	3·4	1·9	25·8
Oxidized Jambad (300 h, 200°C) hydrolysed	67·9	3·5	1·8	26·8

with the minimum quantity of dilute hydrochloric acid, followed by washing by decantation with distilled water. The sample was finally washed in a Buchner funnel, till free from the last trace of hydrochloric acid. It was then air-dried. The sample was then ready for examination.

Carboxylic oxygen

The carboxyl oxygen content was calculated from the base exchange capacity which was determined in the following manner. About 1 g of dry sample was weighed accurately and refluxed with 25 cm³ of 2N barium acetate on a water bath for 1 h. The entire material was filtered and the residue washed with distilled water till free from acids. The filtrate together with the washing was titrated against a standard alkali. From the amount of acid in the solution, the exchange capacity was calculated.

Hydroxyl oxygen

The hydroxyl groups of the samples were estimated by the acetylation method as developed by B. K. MAZUMDAR *et al.*[5]. The phenolic —OH groups were determined by F. UBALDINI's procedure[6].

Carbonyl oxygen

For the estimation of carbonyl groups A. IHNATOWICZ's[7] method was adopted with slight modification. About 5 g of the sample was treated with 5 g of phenyl hydrazine hydrochloride and 5 g of sodium acetate (20 per cent solution). This was refluxed on a water bath for 3 h, filtered and washed successively with 400 cm³ of 1:1 acetic acid–water and 300 cm³ of 1:1 alcohol–water mixture till the washings were free of phenyl hydrazine. The nitrogen content of the phenyl hydrazone was estimated by the Dumas method. From

the gain in nitrogen percentage due to the phenyl hydrazine reaction, the percentage of carbonyl oxygen was calculated.

RESULTS

The ultimate analyses of the samples both before and after hydrolysis with alcoholic caustic potash are shown in *Table 1.* The results of group estimation are presented in *Table 2.* Ring index and aromaticity of oxidized coals are

Table 2. Distribution of functional groups in oxidized as well as hydrolysed coal samples (d.a.f. basis)

Coal sample	Percentage oxygen as —OH by		Percentage oxygen as —COOH	Percentage oxygen as =CO	Total percentage of oxygen as reactive groups	Total percentage of oxygen from elemental analysis	Percentage of oxygen unaccounted for
	Acetylation	Ubaldini's method					
Raw, Jambad	5·4	3·5	0·7	1·5	7·6	13·5	5·9
Raw, hydrolysed	5·5	3·6	1·4	0·7	7·6	13·3	5·7
After 100 h oxidation	5·6	3·7	7·6	4·8	18·0	23·2	5·2
After 100 h oxidation and hydrolysis	6·4	4·7	9·0	3·6	19·0	24·0	5·0
After 200 h oxidation	5·4	3·5	8·9	5·0	19·3	24·5	5·2
After 200 h oxidation and hydrolysis	6·3	4·3	10·7	3·7	20·7	25·4	4·7
After 300 h oxidation	6·9	4·5	9·7	5·3	21·9	25·8	3·9
After 300 h oxidation and hydrolysis	8·0	5·5	11·7	3·8	23·5	26·8	3·3

Table 3. Changes in functional group distribution

Coal sample	Percentage increase of oxygen as —OH after hydrolysis	Percentage increase of oxygen as —COOH after hydrolysis	Increase of oxygen as OH / Increase of oxygen as COOH	Percentage increase in total oxygen hydrolysis	Decrease of percentage oxygen as =CO after hydrolysis
Raw	0·1	0·7	0·14	—	0·8
After 100 h oxidation	0·8	1·4	0·57	0·81	1·1
After 200 h oxidation	0·8	1·8	0·46	0·85	1·3
After 300 h oxidation	1·1	2·1	0·51	1·14	1·5

Table 4. Aromaticity and ring index of Jambad coal (non-hydrolysed) oxidized at 200°C for different periods

Period, h	0	100	200	300
R/C′	0·23	0·22	0·22	0·20
f_a	0·75	0·83	0·84	0·87
H′/C′	0·80	0·73	0·71	0·72
Density	1·31	1·44	1·47	1·48

recorded in *Table 4*. *Table 3* shows the change in oxygen percentage in the form of different functional groups on hydrolysis of the oxidized coals. The ratio of the increase in oxygen as —OH and —COOH on hydrolysis is also incorporated in the same table.

DISCUSSION

Table 2 shows the distribution of oxygen in the form of functional groups at different stages of oxidation. It is apparent that as oxidation proceeds, increasing amounts of oxygen appear in the form of functional groups. From considerations of the elemental composition and distribution of oxygen-containing functional groups, it may be inferred that the oxidation of coal has taken place only to a limited extent. Normally if oxidation of coal is allowed to proceed at 200°C, in the presence of a plentiful supply of air, the amount of hydrogen in the products hardly exceeds 2·5 per cent[2,3] in sharp contrast to the 3·5 per cent obtained in the present case. Moreover, the products of oxidation after 100 to 300 h (at 200°C) normally contain more oxygen in the form of carboxyl groups and less oxygen as hydroxyl groups compared to the data in *Table 2*. Hence the products examined in the present investigation may be looked upon as representing the intermediate stages of oxidation. However, from an examination of *Tables 2*, *3* and *4* the following significant points become apparent.

(*1*) The percentage of total oxygen in oxidized coal increases on alkali treatment.

(*2*) The percentage of oxygen as —OH and —COOH in oxidized coals increases on alkali treatment and the greater the extent of oxidation the more the increase in the oxygen as —OH and —COOH groups (see *Table 3*).

(*3*) The percentage increase of oxygen as —OH and —COOH is roughly in the ratio of 1:2, showing thereby that, on hydrolysis, both the groups are formed in equivalent proportions.

(*4*) The percentage of oxygen unaccounted for decreases gradually with increasing extent of oxidation and this holds good in the case of the hydrolysed as well as the non-hydrolysed samples.

(*5*) The percentage of oxygen as =CO in oxidized coals declines on hydrolysis and the greater the extent of oxidation, the more the decrease in =CO.

(*6*) The magnitude of the increase in oxygen as —OH on hydrolysis is the same whether the —OH groups are estimated by acetylation or by Ubaldini's method. This shows that the —OH groups that are formed on hydrolysis are phenolic in nature.

(*7*) The value of R/C′ (see *Table 4*) decreases almost progressively with increasing time of oxidation. During oxidation the material gets depleted in carbon and hence normally the R/C′ value should go up, provided the condensed aromatic ring structure of the coal remains intact. The decline in the value of the ring index (i.e. rings per C atom) therefore seems to indicate that rings are partially ruptured during oxidation.

In order to formulate a satisfactory mechanism for the oxidation reaction, it is evident that all the factors just enumerated should be taken into account.

Various mechanisms might be proposed in order to explain one or more of the significant facts listed above. The following hypotheses appear more probable and hence their relative merits are discussed.

(*a*) Alkali treatment of oxidized coal might bring about keto–enol transformation. This explains at least partially, the increase in —OH content and decrease in =CO content on hydrolysis, but it fails to explain the formation of the equivalent amount of —COOH groups on hydrolysis and hence this mechanism appears to be untenable.

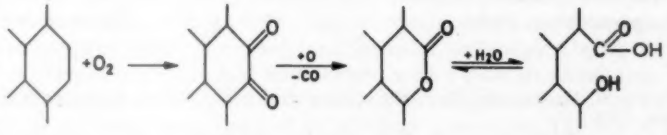
(*b*) The formation of anhydrides on oxidation might explain the formation of —COOH groups on hydrolysis, but it does not offer any explanation so far as other factors are concerned.

(*c*) Keto–enol transformation and formation of anhydride, taken together offer a satisfactory explanation for the formation of —OH and —COOH groups on hydrolysis, but the stoichiometric relation between the two groups cannot be accounted for on the basis of the above hypothesis. Hence, this hypothesis also should be ruled out.

(*d*) If it is assumed that Cannizzaro's reaction takes place during the alkali treatment, then the formation of groups and their stoichiometric relation can be explained. But in Cannizzaro's reaction, only alcoholic —OH groups are produced, whereas in the present case the —OH groups that are formed are phenolic in nature. Hence, this possibility also has to be ruled out.

(*e*) Flavone or lactone structures (e.g. coumarin) might explain the characteristic features of oxidized coals and their behaviour on hydrolysis, but the formation of the flavone type of structure on oxidation seems to be highly improbable and the same considerations apply in the case of the lactone structure of the coumarin type.

(*f*) Lastly, the probable mechanism of oxidation suggested by D. W. VAN KREVELEN[8] should be considered. The mechanisms of oxidation and hydrolysis are evident from the following:



I II III IV

The above represents the different steps involved in the oxidation of coal. Step III represents the final stage of oxidation and the transformation from step III to IV is brought about on hydrolysis, although it is almost certain that the transformation from step III to IV may be brought about to a limited extent even during the course of oxidation, especially in the presence

of humid air. This is supported by the fact that on the progress of oxidation, the value of R/C′ goes down (see *Table 4*). The significant points observed in connection with the study of oxidized coals as well as the hydrolysed coals (see *Tables 2* and *3*) find adequate explanation in the mechanism postulated above. The increase, on hydrolysis, of —OH and —COOH groups in equivalent proportions is evident from the above. Also, the increase of =CO on oxidation and the depletion of =CO groups on hydrolysis, is explained in terms of the above mechanism. The decrease in the percentage of oxygen unaccounted for on hydrolysis is also apparent from the above. The only snag in the above mechanism lies in the fact that according to the above hypothesis, the amount of oxygen unaccounted for should normally go up with the progress of oxidation, whereas the experimental results indicate just the reverse. The only way to reconcile the above contradiction is to assume that coal originally contains oxygen in the cyclic structure and with progress of oxidation, ketone groups are formed giving rise to a structure as shown in step III. This subsequently breaks down with the opening of the heterocyclic rings as shown in steps III and IV. It should also be noted that the experimental values (see *Tables 2* and *3*) are not in exact quantitative agreement with those demanded by the above mechanism, specially with regard to the =CO and oxygen unaccounted for. This is not surprising because the method of estimation of carbonyl groups in coal is not quite satisfactory and secondly the oxygen unaccounted for reflects the cumulative error in the estimation of all the oxygen-containing groups. From the above considerations, it is evident that the mechanism of oxidation as postulated above appears to be satisfactory.

It may be mentioned here that the data of L. BLOM[8] presented in support of the mechanism are curiously inconclusive as well as misleading. They indicate that the additional amount of —COOH and —OH groups that are formed on hydrolysis bear no stoichiometric relation. It should, however, be pointed out that the mechanism of oxidation discussed above merely relates to a limited facet of the phenomenon and does not cover the various concomitant changes involved in the oxidation. To take an example, the formation of a preponderant amount of carboxyl groups that does not find any explanation in the above mechanism can only be explained in terms of the oxidation of peripheral non-aromatic structures present in coal.

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Recent Developments and Notes

PETROLEUM EQUIPMENT

A directory of the French petroleum equipment industry was published for the first time in 1955 and was welcomed with considerable interest both in France and other countries. A second edition of this directory, *Matériels d'équipement pour l'industrie du pétrole*; *édition 1958*, has now been published by Groupement Intersyndical des Fournisseurs de Matériels d'Equipement pour l'Industrie du Pétrole (10 Avenue Hoche, Paris VIII). In a foreword to this volume of over 400 pages, GEORGES PERRET, the president of the administrative council, states that the manufacture in France of equipment for refining petroleum and for the distribution and transportation of its products has kept developing in normal conditions to keep pace with an expanding market, but the manufacturers of drilling equipment have been faced in the past few years with a considerable task to meet increasing requirements due to large expansion in prospecting for, and production of, oil in France and North Africa.

COKE-BURNING APPLIANCES

A Supplement to the Coke-Burning Appliances Handbook was issued in September 1958 by the Gas Council, describing appliances which are additional to those in the fifth edition of the *Coke-Burning Appliances Handbook* published in September 1957 [see *Fuel, Lond.* 1958, **37,** 93]. Twenty five new appliances are described in the supplement and there are many amendments to appliances described in the fifth edition of the handbook.

COKE DESULPHURIZATION

Experiments have been carried out by M. SZUCS and I. SZEBÉNYI to investigate the possibility of producing electrode coke of low sulphur content by the hydrodecomposition of coal and by coking the extract obtained [*Kohasz. Lap.* (*Smelting Pap.*), 1956, **11,** 13; *Hung. tech. Abstr.* 1957, **9** (1), 77; abstract in *Chem. Abstr.* 1958, **52,** 7663]. Subsequent treatment of the extract with hydrofluoric acid resulted in desulphurization to the extent of 23 per cent. Only a mild desulphurizing effect could be obtained by hydrodecomposition in the presence of adsorptive desulphurizing catalysts, alumina being the most effective. The best effect could be obtained with a catalyst containing 2 per cent of chromium oxide and tungsten sulphide in equal amounts, the sulphur content of the coke being reduced to less than 1 per cent. The use of 4 per cent of aluminium chloride during hydrodesulphurization was found to give a similar product of low sulphur content.

L.L.U. TRANSLATIONS BULLETIN

The Lending Library Unit of the Department of Scientific and Industrial Research is introducing a new publication under the title *The L.L.U. Translations Bulletin*. It aims to provide British scientists and engineers who

are anxious to have details of current U.S.S.R. research with up-to-date information on the availability of Russian translations. It will be published monthly and the first issue appeared in January [Her Majesty's Stationery Office, London: price 4*s* (4*s* 5*d* by post). The annual subscription is £2. 13*s* including postage].

The *Bulletin* contains lists of books, journals and scientific papers which are now available or which are being translated and will become available in the near future. One section deals with cover-to-cover translations, a scheme for providing a complete Russian technical journal in the English language, and another gives details of the work being carried out by the National Science Foundation in the U.S.A., with whom the L.L.U. collaborates in this translation scheme. Many translations from America are held in London on microfilm and photocopies may be borrowed.

The *Bulletin* also contains articles on new scientific developments in Russia. These can be followed up in detail with the aid of L.L.U.'s comprehensive collection of Russian scientific literature. It is contemplated that in the future the *Bulletin* will cover translations from other foreign languages.

The Lending Library Unit at Chester Terrace, Regents Park, London, is the nucleus of the new National Lending Library for Science and Technology which will be established at Thorp Arch, near Boston Spa, Yorks., in 1961.

The new library will take over the responsibility for the lending service now provided by the Science Museum Library, which in future will concentrate on serving the needs of the enlarged Imperial College of Science and Technology. It is also taking over some of the literature now held by the Science Museum Library.

The National Lending Library for Science and Technology is one of the two new scientific libraries under discussion. The other is the National Reference Library of Science and Invention, which it is proposed to establish in London as the successor to the existing Patent Office Library.

SUMMARIES OF RESEARCH AT MERL

The Mechanical Engineering Research Laboratory, D.S.I.R., is preparing short summaries of the results of recent research of direct industrial interest to help firms to keep in touch with its work. They will give accounts of work still in progress at MERL as well as the main findings of completed investigations. In addition to a considerable number of engineering subjects covered from time to time will be heat transfer and applied thermodynamics.

In the latest edition of the *MERL Heat Bibliography* there are 12000 references to published papers and books on all aspects of heat transfer and related subjects. It contains references to heat transfer by conduction, convection and radiation; boiling, condensation and evaporation; heat exchangers of various kinds; and physical properties such as entropy, specific heats, thermal conductivity and viscosity. Those who would like to receive copies of the *MERL Research Summaries* or *Heat Bibliography 1955–56* are invited to write to The Director, Mechanical Engineering Research Laboratory, East Kilbride, Glasgow.

OIL DEVELOPMENTS IN IRAN AND INDONESIA

The Iranian Oil Exploration and Producing Co.'s exploratory well Ahwaz No. 6 has now reached a depth of 12742 ft and is the deepest well ever drilled in the southern part of Iran. Drilling is continuing in the hope of an oil strike which might establish the existence of a new field.

This well was the scene of a spectacular fire on 19 April 1958 when gas erupted from a depth of 8093 ft. MYRON KINLEY, the famous firefighter, arrived within two days from the U.S.A. and led the 47-day struggle to get the fire and the well under control.

Another well drilled by this company in the same area, AJ-53, Agha Jari oilfield, was completed on 24 December last at 6832 ft, and has flowed on test at a rate of 40000 barrels of crude oil per day. This indicates a potential yield of upwards of 50000 barrels daily, or about 2½ million tons a year, when put into production, which would make the well one of the most productive ever completed.

A 20 in. diameter pipeline 160 miles long is to be constructed by Shell from its Tandjung oilfield in South Borneo to its refinery on the coast at Balikpapan. It will have a capacity of 2 million tons per annum. The pipeline and ancillary equipment will take three years to build and cost a total of about £18000000. An additional £5000000 will be spent on the further development of the oilfield.

Tandjung oilfield, which was discovered in 1938, yields a highly paraffinic oil, the pumping of which involves many technical problems. These have been under examination for several years and in the new pipeline oil will be mixed with about 30 per cent water and pumped in suspension; in this way it will not be necessary to provide heating stations along the pipeline.

HUMIC ACID

The Plant Phenolics Group of Food Investigation, University of Cambridge and Department of Scientific and Industrial Research, are to hold an International Symposium on 'Humic Acid', in the Department of Chemistry, University College, Dublin, on Thursday and Friday, 10 and 11 September 1959. Further information may be obtained from the Honorary Secretary, Dr T. SWAIN, Low Temperature Research Station, Downing Street, Cambridge.

EMBRYONIC PETROLEUM

A remarkable oil deposit has been discovered in the delta of the Orinoco River in Eastern Venezuela and is now being examined by scientists from three affiliates of Standard Oil Company (New Jersey). The oil is only five to ten thousand years old, whereas the age of normal petroleum is probably more than ten million years. This is said to be the only occasion known when the collection of hydrocarbons in a stratigraphic trap has been observed in process of creating an oil reservoir. This deposit thus provides the most conclusive evidence so far that the oil-forming process is still going on.

A fully equipped laboratory has been set up in the field for the analysis of sediments before any deterioration can occur. All cores are being examined in

the field laboratory and some will be sealed with plastic and sent to the U.S.A. for further studies. Samples for geochemical research are being canned in alcohol to protect them against decomposition by bacteria [*Inst. Petrol. Rev.* 1959, **13**, 12].

PREDICTING COKE QUALITY

H. McKELLAR, W. BURNS and V. GIEDROYC, of Colvilles Ltd, have written a paper on the relationship of the properties of coals and coal blends with the quality of coke produced [*J. Inst. Fuel*, 1958, **31**, 528]. The object of the research was to obtain, by statistical methods, some fundamental basis for blending Scottish coals for coking, data relating to 30 coal types being used. Two approaches were made, one using coke obtained by the Jenkner small-scale carbonization apparatus, and the other using the industrial coke made at Colvilles coke oven plants. The object of the statistical analyses was to explain the quality of the coke in terms of the coal properties. The coal properties considered were: (*i*) volatile matter content on dry, ash-free basis, (*ii*) maximum fluidity, (*iii*) plastic range determined by the Gieseler plastometer, (*iv*) British Standard Swelling Number, (*v*) petrographic composition. The coke quality was expressed by the conventional indices and also by a 'quality index' incorporating the results of both the shatter index and Micum drum tests.

The maximum fluidity of the coal was found to be the factor having the largest effect on the coke quality. It was shown, however, that the variation in the properties measured could account for only about 40 per cent of the total variation in coke quality. Therefore a fresh approach to testing the coking properties of coals appears necessary. The results of the investigation are regarded as justifying the introduction of measurements of the plastic properties of coals and coal blends on a routine basis.

FUEL RESEARCH IN INDIA

The *Report* of the Director, Dr A. LAHIRI, of the Central Fuel Research Institute of India, for the year 1956–57, has recently been received in this country [Council of Scientific and Industrial Research, April 1957; Jealgora, Dhanbad, Bihar].

The emphasis during this period has been on coal survey, preparation and carbonization, to meet the needs of public and private industries in the second Five Year Plan and for future developments. The Carbonization Section has been specially concerned with investigations on the carbonization of coal blends for producing metallurgical coke for the projected steel plants and the Durgapur coke oven project. During the period under review one of the most important advances has been the commissioning of the pilot high-temperature carbonization plant at the Institute in which large-scale tests can be carried out.

The target for the production of coal in India is 60 million tons per annum by 1960, which is an increase of 23 million tons on the production in 1955. At present 80 per cent of the total coal output and the whole amount of coking coal are obtained from the Bengal and Bihar coalfields, in the eastern part of

the country. With the spread of industries, particularly the new large industrial plants, it will be necessary to increase the production from outlying coalfields in order to relieve the burden on transport and to supply coal at the cheapest rate to the newly established industries.

There are five coal survey stations: Jharia, Central India, Bokaro–Ramgarh–Karanpura, Assam, and Hyderabad, and accounts are given of the work at these stations. Work is also described in connection with the sampling of coal, its geology and petrology, preparation and handling, and with coal tar and by-products, combustion engineering, fluidization and gasification, synthetic oil, fundamental studies related to coal, analysis and testing of coal and its by-products. There were 48 papers published during the period by members of the Institute staff, and a further 14 papers were submitted for publication. Seventeen reports were also prepared.

PETROGRAPHIC STUDY OF COAL

In connection with the intensive physical and chemical survey of the coal resources of Australia which is now being carried out, considerable attention is being paid to the petrography of these coals. The techniques which are being used for this purpose in the Coal Research Section, C.S.I.R.O., Chatswood, N.S.W., have recently been described in a report by G. H. TAYLOR and W. ZEIDLER [Reference M. 146, October 1958].

The types of coal samples used for this petrological work are polished blocks, thin sections of lump material, polished grain mounts, and thin sections of grain mounts. Many of the methods of preparation of these various types of samples of brown coal, bituminous coal and coke have been evolved in the Coal Research Section. Methods are also described for the preparation of relief-free surfaces and of small objects, and for the impregnation of loose grains. In addition to petrographic microscopes, the electrical point counter and the Berek slit microphotometer are used. Information is given about impregnants and mountants for grain mounts, embedding media for small objects, cements, grinding and polishing materials.

PORE STRUCTURE OF COKE

A. CAMERON and W. O. STACY, of the Coal Research Section, C.S.I.R.O., Chatswood, N.S.W., have described an investigation on the pore structure of coke during carbonization and gasification [*Austral. J. appl. Sci.* 1958, **9**, 283]. The work was undertaken as part of a research on the influence of pore structure upon gasification rates at different temperatures. Previous work in this field has been concerned mainly with the micropore (4 to 25 Å diameter) structure of coke, but the existence had also been shown of macropores in active carbons with diameters of 10000 to 40000 Å.

In the present work the changes in the pore structure of cokes from coals carbonized at temperatures in the range 400° to 900°C, and gasified for various lengths of time with steam, were investigated by studying the changes in internal surface area, apparent specific volume in various liquids, and penetration of mercury under pressure. The volume of pores within definite size ranges was calculated from the apparent specific volumes determined in water, ethylene glycol, benzene, tri-*o*-cresyl phosphate, and silicone oil. The

internal surface areas of the coke samples were determined by the adsorption of nitrogen, water, acetone and *n*-hexane. The nitrogen adsorption isotherms were obtained by the volumetric method and those for the other adsorbates by a gravimetric method using a modified McBain and Bakr adsorption balance.

It was found that there are two distinct pore systems in the coke structure which persist during carbonization: (*a*) macropores, with entrances in the range 400 to 130000 Å diameter, and (*b*) micropores with entrances less than 10 Å in diameter. The majority of entrances to the macropores have diameters in the region of 7600 Å. The macropores contain many constrictions the number of which increases with carbonization temperature up to 700°C, and then remains constant.

The micropores are of two types: (*a*) those approximately cylindrical in form and less than 10 Å diameter, and (*b*) those much larger but with constricted entrances less than 10 Å. As the carbonization temperature increases the accessibility of both types of micropores decreases until at 900°C, of the liquids used, only water can penetrate.

During gasification of coke at 800°C with steam, the reaction occurs at all the internal surfaces of the coke and constrictions in the macropores and micropores are gradually removed. The micropore structure becomes increasingly accessible to larger molecules.

THE EFFICIENT USE OF FUEL

The first edition of *The Efficient Use of Fuel* was published in 1944, in the stress of war conditions when fuel economy was an acute national need. It was a cooperative effort by technologists associated with the Education Sub-Committee of the Fuel Efficiency Committee of the then Ministry of Fuel and Power.

The second edition [Her Majesty's Stationery Office: London, 1958; *vi* + 888 pp; 35*s*] has now been published and is a complete revision in detail and so largely rewritten that it is practically a new work. The preparation has been carried out by leading fuel engineers and fuel technologists working under the control of the Fuel Efficiency Committee of the Ministry of Power. The new edition incorporates the results of developments in the science and practice of fuel technology over the past fourteen years.

The chapters on Heat Transmission, The Flow of Fluids, Water Treatment, Space Heating, Drying and Conditioning, Heat Balances, and Instrumentation have been almost completely rewritten and that on Coal largely rewritten and brought up to date with reference to the National Coal Board's Code Number Classification. Callendar's Steam Tables replace those of Keenan and Keyes, in which respect the new edition is now in accord with the companion volume *The Efficient Use of Steam*. The results of the work of the British Standards Institution Committees on Sampling and Analysis of Coal and Coke have been used in revising the appropriate chapters.

Among other new features are a comprehensive bibliographical reference list after each chapter, a 2-colour 'throw-out' psychrometric chart and an appendix of Units and Conversion Factors.

EFFICIENCY OF THE MINING INDUSTRY

The seventh Cadman Memorial Lecture was delivered to the Royal Society of Arts in London by H. A. LONGDEN, Director-General of Production, National Coal Board, and President, Institution of Mining Engineers, in November 1958. The subject was 'Improving the Efficiency of the Mining Industry'.

Planning in Great Britain in the past few years has been based on the expectation of a ready sale for 216 and 228 million tons of deep-mined coal in 1960 and 1965 respectively. These amounts, compared with a production of 198 million tons in 1948, pointed to the need for a considerable expansion of effort. By 1956, deep-mined production amounted to 210 million tons and since then home consumption has fallen, so that it is expected that for 1958 it will be 16 million tons below the 1956 level.

Increases in demand for coal are for gas-making, electricity and coke ovens. The domestic consumption of coal and gas will probably decline in the future, and an increased demand for coal from general industry cannot be expected, owing to the increasing use of fuel oil. The decrease in consumption of coal by the railways reflects the progress of the programme of dieselization and electrification.

In America, despite the existence of the huge oil industry, coal maintains the greater part of the market for electrical power generation, and has *more* than held its own against oil in the past decade. The lecturer considered that the small foothold that oil has gained in electricity generation is not at present justified on economic grounds, nor will it be in the future, as the small, uncleaned coal required by power stations is the fuel which modern machines in pits can produce most cheaply and efficiently.

It must be stressed that the American coal industry has only held its own in the face of intense competition from indigenous oil by achieving an efficiency of production in terms of output per manshift which, making all necessary allowances for our more difficult conditions, has not been matched by our own industry.

The lecturer reviewed the great progress in the past few years in increasing efficiency at the coal face by mechanization, pointing out that the percentage of output got by power-loading today is still only 28 per cent and even within that maximum efficiency is not yet achieved. Sections of the lecture were devoted to the use of the coal cutter, the face belt conveyor, the Meco–Moore cutter loader, the armoured flexible conveyor, the Anderton shearer loader, cyclic mining, yielding hydraulic props, powered or 'self-advancing' supports, and the trepanner.

The above equipment has introduced a new conception of 'continuous' mining in which, in contrast to the cyclic system, all the various jobs on the coal face are done simultaneously in the same shift, and in which in theory, therefore, every shift can be a coaling shift. The principal obstacle to full continuous mining at present is the speed of road-making, or ripping. The solution of this problem depends on the invention of a ripping machine which will eliminate the use of explosives at the ripping lip and will, in one operation, get down the requisite amount of dirt and stow it in the gateside packs.

Steady progress is being made in the application of method study and work measurement to the problem of setting a reasonable task to which a reasonable wage can be attached. The objective approach offered by these techniques will give a consistently fairer deal to employer and employee alike and, at the same time, ensure more efficient utilization of valuable machinery.

THERMAL PROPERTIES OF CARBONACEOUS MATERIALS

A paper was presented to the Division of Gas and Fuel Chemistry of the American Chemical Society at its meeting in September 1958 at Chicago, by J. D. BATCHELOR, P. M. YAVORSKY and E. GORIN, of Consolidation Coal Co., Library, Pa, on measurement of thermal properties of carbonaceous materials.

Three parameters of interest for the thermal processing of carbonaceous materials were studied. Heat capacity measurements were made on a bituminous coal from the Pittsburgh seam and its low temperature char produced by fluidized carbonization at just over 500°C. The mean specific heat capacity from room temperature to temperatures of 260° to 480°C was found to range from 0·34 to 0·41 for the coal and from 0·28 to 0·31 for the char. These measurements were made in a simple high temperature calorimeter. The thermal conductivity was determined of briquettes consisting of 25 per cent coal, 63·5 per cent low temperature char and 11·5 per cent pitch. The values obtained were found to follow a pattern similar to coal being coked, showing a 20-fold increase in value from room temperature to hot coke temperature. The conductivities were measured by a direct method using a compensated conductometer. An estimation was also made of the surface film heat transfer coefficient from a fluidized heating medium to an aluminium sphere. An unsteady state system was used as the measurements can be rapidly made. Values for the heat transfer film coefficient of about 30 B.Th.U./h. ft².°F were obtained and assuming that the nature of the surface of the sphere is unimportant to the result, the values are regarded as being applicable to carbonaceous briquettes.

In a companion paper presented to the same meeting, P. M. YAVORSKY, R. J. FRIEDRICH and E. GORIN discussed heat transfer and associated effects in the carbonization of coal–char briquettes, using the heat transfer film coefficients referred to above. Temperature/time patterns for the carbonization were computed with an electronic digital computer for various briquette sizes, transfer coefficients, and two shock heating methods, hot flue gas and hot fluidized solids. Combination of the thermal patterns with experimental briquette expansivity data has yielded information on the relative magnitude of thermal stresses in briquettes undergoing carbonization. Excessive stresses lead to deleterious briquette fracturing. The results obtained are of value in defining the physical conditions and dimensions in the design of carbonization units for a continuous process to produce formcoke suitable for blast furnace use.

NEW THERMAL REFORMING PROCESS

The Municipal Gas Works at The Hague is contemplating the adoption of a new thermal reforming process for the conversion of oil refinery gas to town gas. It is claimed that in the city's gas works a method has been devised for the

reforming to be accomplished without the deposition of carbon in the reactor. This would make it possible to operate the process continuously instead of cyclically. The reaction mixture, possibly refinery gas plus a hydrogen-rich recycle gas, is pretreated at 800° to 850°C for approximately 0·5 sec in order to convert the higher hydrocarbons into methane and ethane. Then the gas mixture is heated to 1 200° to 1 400°C and steam is added. Tests have indicated that existing gas works equipment can be adapted to the reforming process with savings in labour and maintenance costs and a capacity increase of 65 per cent [*Chem. Engng*, 1958, **65** (23), 61].

NEW LIGNITE GASIFIER

The U.S. Bureau of Mines is about to start up a new pilot plant at Grand Forks, N.D., for the pressure gasification of lignite with steam and oxygen to produce synthesis gas for making, amongst other products, liquid fuels and town gas. In North Dakota there are abundant supplies of lignite, virtually untapped.

The plant is essentially the Lurgi fixed-bed gasifier, but differs from conventional units in that it will operate under slagging conditions. This will permit operation with a lower steam/oxygen ratio, thus giving higher overall thermal efficiency and increased gas-making capacity.

The gas generator has a fuel-bed cross section of 1·5 ft^2. It is divided into four sections so that the height of bed can be varied for different fuels and processing conditions, between 6 and 15 ft.

The most important problem connected with the satisfactory operation of the plant will be the development of a device for tapping slag under a pressure of 700 lb/in^2. A lock-hopper has been devised in which the slag is quenched in water, granulated and accumulated for intermittent discharge to atmospheric pressure as a slurry [*Chem. Engng*, 1958, **65** (22), 52].

SULPHUR IN FUELS

At a meeting of the Division of Gas and Fuel Chemistry of the American Chemical Society in September 1958 at Chicago, a symposium was presented of papers on sulphur and ash in fuels and their products. H. J. Rose contributed a paper on the percentages of ash, total sulphur and sulphur forms in U.S.A. coals; M. Deul, on the biochemical and geochemical origins of ash-forming ingredients in coal; W. van Hees, on the separability of pyrites particles in some pulverized coals; W. van Hees and E. Early, on a modification of Mott's method for the determination of pyritic sulphur in coal; and T. S. Polansky and E. C. Knapp, on the effect of hydrogen sulphide on the sulphur content of bituminous coke at 800° to 1 000°C.

GASIFICATION OF COAL

In the University of Columbia, New York, the conversion of coal into methane by the use of a powerful source of radiation is being studied. A 9 kg mass of radioactive cobalt of 1 400 curies is used. The investigation is being subsidized by the Consolidated Natural Gas Co. of New York. The coal is heated and submitted to high pressure for the irradiation process. The radiation assists in the decomposition of the coal and acts catalytically in a hydrogenation

reaction in which the coal decomposes into gases consisting chiefly of methane [*Chim. et Industr.* 1958, **80,** 825].

NEW MOTOR FUEL

Nitroparaffins are being investigated by E. S. STARKMAN, professor of aeronautical engineering in the University of California, Berkeley, as fuels for diesel and spark-ignition engines. It is said that their use in these engines produces double the normal power obtained by the combustion of hydrocarbon oils, and that their particular property is the release of part of their oxygen to the combustion process, thereby increasing the pressure in the cylinder. Nitromethane appears to be the most interesting of the compounds. It is considered that with some minor modifications, spark-ignition engines could use nitromethane with entire safety and without pre-ignition occurring. In the operation of diesel engines the tendency for pre-ignition to occur would be advantageous [*Chim. et Industr.* 1958, **80,** 831].

FLUIDIZED CARBONIZATION OF COAL

CERCHAR has put into operation a fluidized process of coal carbonization. Semicoke or granular coke of very uniform quality can be produced. Coals with very high volatile contents can be used in this process. The solid product can be used as an anti-fissuring material to enable non-coking fines to be coked, as with Lorraine coals.

The process, which extends the range of Lorraine coals that can be coked, has been worked on the scale of 100 kg/h in the CERCHAR laboratory at Verneuil-en-Halatte, and on a scale of 1 tonne/h at the Marienau experimental station. Plans have been prepared for the construction of an industrial unit of 10 tonnes/h [*J. Usin. Gaz*, 1958, **82,** 569].

STEAM TABLES

At the fifth International Steam Table Conference held in London, in July 1956, an International Coordination Committee on the Properties of Steam was set up. The first meeting of this Committee was held in London in 1957 and the second meeting took place in Moscow last July. Germany was represented by Professor Dr-Ing. H. HAUSEN, Professor Dr-Ing. E. SCHMIDT, and Dr-Ing. K. R. SCHMIDT; Great Britain by Professor D. M. NEWITT, Professor J. SMALL, and Messrs W. W. CAMPBELL and E. J. LE FEVRE; America by Professors F. G. KEYES, J. H. KEENAN and B. H. SAGE; Russia by Professors V. A. KIRILLIN, N. B. VARGAFTIK, M. P. VUKALOVICH, and G. ARMAN. An account of this meeting has recently been published by E. SCHMIDT [*Brennst.-Wärmekr.* 1958, **10,** 553].

At the meeting H. HAUSEN presented a paper dealing with a proposal for setting up an international steam table which will be valid for all countries. Up to the present the Conferences have only dealt with skeleton tables containing values and tolerances for the enthalpy and specific volume of steam.

Since it is very difficult to find an equation of state which is sufficiently accurate to cover the whole range of state, the author shows how a steam table of consistent values can be constructed by a step process representing approximate solutions of the thermodynamic differential equations. The values so

obtained are very close to those of the skeleton tables and also to the generally accepted results of experimental research [*Brennst.-Wärmekr.* 1958, **10,** 557].

FLUID FLOW MEASUREMENTS BY ULTRASONICS

C. KNAPP has written a very full account of the physical basis of the use of ultrasonics for the measurement of velocity of flowing fluids and discussed the various possibilities of this technique [*Voith Forschung u. Konstruktion*, No. 3 (August 1958) 1 to 40]. In the experimental part of the paper a new method using this principle is described.

Using a rectangular channel of 1 m width, with a fluid whose velocity was in the range 0·06 to 0·9 m/s, the errors in flow measurement, even with pronounced side and base currents, were in the range $\pm$ 0·4 per cent.

In a water-powered apparatus with a flow up to 8 m³/s the measurements obtained by this method differed by +0·3 to +0·8 per cent from the values obtained by a rotameter. The whole determination can be conducted from outside the flowing fluid, so that there are no measuring instruments to affect the flow. An integrated measurement over a longer period of time, when the flow conditions are of a fluctuating character, is found to give a good average value.

CHEMICAL ENGINEERING

A recent issue of *Génie Chimique* (November 1958), the monthly supplement to *Chimie et Industrie*, was devoted specially to articles on the general subject of chemical engineering, with the particular object of defining the tasks of this branch of technology and of reviewing trends and developments in techniques. Two papers on these subjects are by A. ZUNDEL, who has also contributed a comprehensive German–French dictionary of chemical engineering terms, covering 32 pages.

COAL PLASTICITY IN COKING

D. W. VAN KREVELEN and F. J. HUNTJENS, of the Staatsmijnen in Limburg, Centraal Laboratorium, Geleen, Netherlands, have made an important contribution to the subject of the plasticity of coal during carbonization [*Chim. et Industr.* 1958, **80,** 234]. One of the essential problems of this subject is whether the material which passes through the plastic state is originally present in coal or is formed during coking. The investigation which is described in the present paper is the determination, by an indirect method, of the nature of the viscosity of undecomposed coal above 400°C.

The vitrinite of coking coals is entirely soluble in tar pitch at 200°C. The viscosities of tar pitch and of solutions of coal in tar pitch were measured in different types of viscometers at different temperatures in the range 10^{10} to 10^{3} poises. From the temperature at which the viscosities of the solution and of the tar pitch are the same, the temperature at which the coal has the same viscosity was determined by extrapolation. This method was checked by measurements on tar pitch fractions with different viscosities.

The viscosity so determined is that of undecomposed coal as the temperature did not exceed 200°C. On comparing the viscosity obtained in this way with the viscosity of coal during carbonization, as determined by means of a Gieseler plastometer, it is concluded that the degree of plasticity occurring

during the coking process must be primarily ascribed to the character and quantity of products formed during decomposition.

UNDERGROUND GASIFICATION PROJECTS

The National Coal Board have announced that, from 31 May, further experimental work at Newman Spinney, near Chesterfield, on the gasification of coal underground will cease.

This work was on thin and faulted seams which would not be mined in the normal way. It has been calculated that if development were successful, gas from such seams, used to run a generating station, would cost about 3*d* a therm. This is only just competitive with normal methods of producing power, and in present circumstances in this country the Board have felt that continued experimental and development work would not be justified.

Humphreys and Glasgow Ltd, the company which has been in charge of the project for the National Coal Board since March 1957 with the objective of providing gas for a 3·75 MW generating plant, have carried out a great deal of experimental work, and gas is due to be delivered shortly to the pilot plant at Newman Spinney. Two methods are being used, one developed entirely in Britain, and the other adapted from a Russian system as a result of the exchange of visits by experts of the two countries last year. It is believed that in favourable geological conditions, gas produced underground could be competitive with any other form of power station fuel.

It has also been announced recently that the U.S. Bureau of Mines will close down its experimental underground gasification project at Gorgas, Ala, within a few months. Three methods have been tried on this site: (*i*) simple preliminary mining to prepare the coal seam, (*ii*) passing a heavy electric current through the bed to effect carbonization and create a porous condition, and (*iii*) hydraulic fracturing, as used in the petroleum industry. None of these methods was found to produce gas sufficiently cheaply.

REACTIVITY OF COKE

A. F. BOYER, G. DURAND and P. PAYEN, of Laboratoire du Centre d'Etudes et Recherches des Charbonnages de France, have published a paper on the reactivity of cokes towards carbon dioxide, under the conditions of use in the cupola furnace [*Chim. et Industr.* 1958, **80**, 220].

The results obtained in this investigation confirm a view put forward previously by these authors [*Rapport annuel du CERCHAR, 1955*, p 155] that the reactivity of coke towards carbon dioxide in a cupola furnace is *chiefly* controlled by diffusion of the gas into the pores of the coke, rather than by chemical reaction involving the oxidation of iron carbide. Simple laboratory equipment is described in which pieces of coke between 10 and 100 g in weight can be gasified at temperatures up to 1 500°C. For pieces weighing about 20 g the gasification was found to take place about 1 200°C by a diffusion process as in a cupola furnace. The method used is recommended for the routine assessment of industrial cokes. Under these conditions the relative reactivity of various cokes is not the same as when diffusion processes are absent. The reactivity of cupola coke should be measured at the temperature of its use in the cupola furnace, and with unabraded pieces. The

parameter most important for predicting the performance of a furnace is the loss in weight after gasification and abrasion rather than after gasification alone. Partly gasified coke undergoes mechanical disintegration which varies greatly from sample to sample.

In another study of the reactivity of coke, M. MOUTACH and H. GUÉRIN, of the Laboratoire de Chimie Minérale Industrielle de la Faculté des Sciences de Nancy et de l'Ecole Nationale Supérieure des Industries Chimique, have continued their investigations on this subject and have presented an account of experiments on the reaction between coke and steam at high temperature [*Bull. Soc. Chim. Fr.* **1958**, 1008]. The particular objective of this work was to study the variations of reactivity of cokes during their gasification. The method used was that of continuous determination of the speed at which gasification occurs during the complete gasification of the coke sample. An account is given of the experimental precautions taken in regard to continuous gas analysis, and constant and continuous current of steam.

The relative importance of temperature, concentration and rate of delivery of steam, height of coke bed, and size of coke particles, was determined for six cokes, and the optimum conditions were deduced for the reactivity determinations. The determination from the experimental results of the specific velocity of gasification as a function of the amount of coke consumed, confirmed the importance of the variation of reactivity during the progress of combustion of the coke. This indicates the necessity of relinquishing the determination of the initial reactivity of coke as a criterion of practical value and also emphasizes the decided differences in the behaviour of cokes of various types. An examination has been undertaken by these authors of the evolution of the porous structure of cokes undergoing gasification.

TOWN GAS FROM REFINERY GAS

The use by the Southern Gas Board of refinery gas from the Fawley refinery of the Esso Petroleum Co. Ltd, was the first of its kind in the United Kingdom, although some had been used for the cold enrichment of producer gas and blue water gas. Experiences in the production of town gas from this refinery gas since July 1957 have now been described in a paper presented to the 24th Autumn Research Meeting of the Institution of Gas Engineers last November, by W. F. THORNE, R. K. HARRISON and J. R. FAIRMAN [*Publ. Instn Gas Engrs, Lond., No. 536* (1958)].

Existing water gas plants were modified in order to carry out reforming of the refinery gas and it has been found that this can be accomplished successfully both from the technical and economical points of view. The gas made is satisfactory in composition and is interchangeable with other gas produced in the area. The process makes a substantial reduction in the carbon monoxide and organic sulphur contents of the gas. The composition of the refinery gas is not critical to the process and complete flexibility can be maintained. The process produces no effluent problem. Naphthalene arising from the reforming process gave rise to greater difficulties in the distribution system than had been foreseen. Consequently for some time, until a naphthalene washer could be installed, the reforming process was operated at slightly lower temperatures than the optimum values.

The increased output from the water gas plants when reforming refinery gas necessitated additional alternative gas-making plant so that full advantage could be taken of the maximum quantity of refinery gas available. Catalytic oil gas plant was used for this purpose, with either refinery gas or oil as feedstock, according to the most economic prevailing conditions.

OIL FROM COAL

The Fuel Research Board has recommended that only two main items of research now being undertaken at the Fuel Research Station at Greenwich should be transferred to the new laboratories now nearing completion at Stevenage. These are the programmes of work concerned with the measurement and abatement of air pollution, and with the synthesis of oil from coal [*Fuel Research 1957*. Department of Scientific and Industrial Research: Her Majesty's Stationery Office, London, 1958]. Work on the latter is to be continued at Stevenage up to pilot-plant scale and arrangements for moving are being made so that as little delay as possible is caused to the investigation.

The work of the Fuel Research Board on the liquid-phase technique for the synthesis of oil from coal by the Fischer–Tropsch process is linked with the work that is being undertaken by industry under contract from the Ministry of Power to examine the economics of combining a new method of gasification with the best synthesis technique.

The main lines of investigation in this field now comprise the development of cheap but active and durable catalysts for the synthesis reaction and the solution of the chemical engineering problems peculiar to the liquid-phase process. Increased effort is being directed to fundamental studies of catalysis. Further work has been done on promoters for mill-scale catalysts, and also on the development of inexpensive precipitated iron catalysts. The composition of the synthesis gas in relation to catalyst performance is also being studied. In fundamental work, an account is given in the report of experiments relating to the increase in activity of certain catalysts when subjected to gamma radiation. X-Ray examination of iron catalysts is being used in connection with the effect of treatment with alkali on the activity of mill-scale catalysts, and an investigation is proceeding on the surface structure of catalysts. The use of chromatographic methods for the examination of synthesis products is being continued with emphasis on the investigation of the effect of reaction conditions on the distribution of structural isomers.

STRUCTURAL ANALYSIS OF OILS

The various parameters used in methods of structural analysis of petroleum fractions were originally intended for application to fractions with sulphur contents only up to 2 per cent. It is becoming important, however, to know if these methods are applicable to oils with greater sulphur contents, at least up to 7 per cent. For this purpose a study of the subject has been undertaken by A. CAMISA and C. A. FRATTA, of the Laboratori del Servizio Geochimico dell' AGIP Mineraria [*Riv. Combust.* 1958, **12**, 815].

The well-known methods of structural analysis due to H. I. WATERMAN and his co-workers have been examined to ascertain whether the corrections introduced into the parameters are valid for oils with higher sulphur contents.

The experimental determinations and calculations were carried out on sulphur-free fractions and blends with sulphur contents in the range for which the original methods are valid. The data obtained on these blends were extrapolated for fractions with higher sulphur contents. It was found that the corrections introduced in the original methods are applicable to fractions with sulphur contents up to 7 per cent. It was also ascertained that for such fractions the C_A per cent, R_A and MW do not require a correction for the increased sulphur content.

COAL PREPARATION

At the Third International Conference on the Preparation of Coal, held in June 1958, at Liège, a paper was read by A. JUROVSKI and V. GOROSHKO on the use of radioactive isotopes and radiations in investigations on coal preparation and in full-scale practice. A radiometric separator, of fairly high capacity, has been devised in Russia which makes possible the automatic extraction of rock from raw coal. Gamma radiation of 0·04 to 0·06 MeV is involved in the process. Radioactive methods are also applied in studying the mechanism of separation of particles of coal and rock by gravimetric methods and in measuring the viscosity of dense coal suspensions and opaque liquids [*Ann. Min. Belg.* **1958**, 1041].

At the same conference K. ASAI and N. SASAKI described the use of ultrasonics in the treatment of slurry. Using a barium titanate transducer rapid and complete flocculation of coal particles has been obtained on a semi-industrial scale of 6 to 10 m^3/h. Pre-treatment by ultrasonic irradiation of slurry which is to be floated can increase the capacity of a flotation plant by 50 to 70 per cent [*ibid*, 1042].

W. A. KIRKBY

MOISTURE AND CALORIFIC VALUE OF YALLOURN BROWN COAL

The heading of the last column of *Table 7* which appeared on page 403 of *Fuel* for October 1958 should read: 'Air-dried' coal. The words 'in nitrogen' did not appear in the proof. This ambiguity arose in the last stage of preparing the article for machining due to a misunderstanding; it is removed at the request of Miss Rossiter, author of the article.

AROMATICITY OF COAL

B. K. MAZUMDAR, S. K. CHAKRABARTTY and A. LAHIRI have now supplied an additional legend which should have appeared with their *Figure 2* on page 118 of the January issue of *Fuel*. It is as follows: ● From oxidation studies[6,7]; + From D. W. VAN KREVELEN *et al.*[3]; □ van Krevelen's, as revised by the present authors from *Figure 1*; △ From i.r. analysis[2]; ○ From pyrolysis[14]. The same authors wish it to be known that the heading in the last column of *Table 1* on page 113 of the January issue of *Fuel* should be 'C_{har}', referring to hydroaromatic carbon.

THE INTERNATIONAL BRIQUETTING ASSOCIATION

Present members of the International Briquetting Association represent the industry in the U.S.A., Canada, England, France, Germany, Switzerland,

Belgium, New Zealand, India, Japan, Mexico, Hungary and South Africa. The secretary is NEAL RICE, of the Natural Resources Research Institute, University of Wyoming, Laramie, Wyoming, U.S.A., who will be glad to supply details of the Association's activities. It is announced that the 1959 (Sixth) Biennial Briquetting Conference will be held at Glacier Lodge, Glacier Park, Montana, U.S.A. from 24 to 26 August.

GORDON RESEARCH CONFERENCES

The Gordon Research Conferences for 1959 will be held from 15 June to 4 September at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire and Kimball Union Academy, Meriden, New Hampshire.

Individuals interested in attending the conferences are requested to send their applications to the Director at least two months prior to the date of the Conference. All applications must be submitted on the standard application form which may be obtained by writing to the office of the Director. The Board of Trustees of the Conferences has established a fixed fee of $100 for attendance at each Conference. For all information write to W. GEORGE PARKS, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island.

The Gordon Research Conferences on the Chemistry and Physics of Coal will take place at New Hampton School, New Hampton, New Hampshire, under the chairmanship of HENRY C. HOWARD, with JOHN MACKAY as Vice-Chairman, covering the following subjects: 22 June: Functional groups in coal; 23 June: Low-temperature reduction reactions; 24 June: Optical and mass spectra; 25 June: Structural methods in the study of coal and related products; 26 June: Round table discussion and plans for 1960 conference.

COMBUSTION AND FLAME

The March issue of *Combustion and Flame* included *Notes* on the following subjects, which may be of interest to readers of *Fuel:*

Flame research at IJmuiden
Carbon index of fuel gases
Explosion and fire hazards in lighting
Measurement of smoke
Improved boiler efficiencies
Recent trends in the industrial use of gas
Cyclone combustion
Sulphur trioxide in flue gases
Flame evaluator

OVERSEAS CORRESPONDENTS' NOTES

The Editor is grateful for the following information on matters of present interest relating to the fuel science field. Dr D. S. Montgomery has kindly supplied the notes on Canada, while those on India were contributed by Dr J. W. Whitaker, those on Italy by Professor C. Padovani and those on Japan by Dr Akira Shimomura

CANADA

Past meeting

An informal Commonwealth Specialist Conference on Fuel Research was attended by delegates from the Commonwealth on 6 September in the library of the Canadian Institute of Mining and Metallurgy in Montreal. The agenda was mainly concerned with organizational matters, but the meeting devoted some time to discussing details concerning the publication of reviews of topics in fuel technology, Commonwealth facilities for fuel research, and arrangements for exchange of both personnel and of scientific communications.

Future meetings

The next meeting of the Mining Society of Nova Scotia will be held at the Keltic Lodge, Ingonish Beach, N.S. on 2, 3 and 4 July.

The Dominion–Provincial Coal Research Meeting is to take place in September at Saskatoon on the campus of the University of Saskatchewan under the auspices of the Saskatchewan Research Council. The Chairman will be the director of the Saskatchewan Research Council, Dr T. E. WARREN.

Recent developments

The research project on coal-burning gas turbines conducted at McGill University under the direction of Professor D. L. MORDELL has been terminated. The project was supported financially by the Department of Mines and Technical Surveys. The equipment and instruments have been turned over to McGill University to encourage graduate engineering research in Canada in the field of combustion. A complete engineering report describing the technical aspects of this project is being prepared by Dr J. W. STACHIEWICZ of McGill University, and it is expected that it will be issued shortly by the Department of Mines and Technical Surveys, Ottawa.

Both the Canadian National Railways and Canadian Pacific Railway have converted almost 90 per cent of their locomotives to diesel electric engines. As the same type of diesel engine is used in pumping oil on the trans Canada pipeline service, the railways are seriously considering a research programme to study the burning of certain types of crude oils in locomotive service in Western Canada.

A. V. Roe Canada Ltd has acquired the controlling interest in the Dominion Steel and Coal Corporation Ltd, which was the major coal producing company in Eastern Canada. As the result of this change in ownership a re-examination of the principal coal markets is being made and a research programme is being formulated to expand these markets.

A new method of recovering heavy oils and bitumens from deep beds of bituminous sand has been proposed by the Richfield Oil Co. This proposal has been made with particular reference to certain bituminous sand deposits which they have recently discovered at the southern extremity of the bituminous sand area of Northern Alberta. These deposits are approximately two hundred feet in thickness and are situated under an overburden of approximately 1000 ft. It is proposed that an atomic device be exploded at the interface between the bituminous sand and the Devonian limestone upon which these sands rest. The heat generated by this device would heat the oil to the point where it could be made to flow to a collecting point. A request has been made to the Canadian Government to form a technical committee to look into the soundness and safety of conducting an experiment to establish the value of this type of oil recovery. As there are numerous political and technical questions concerning such an experiment it is expected that a considerable period of time will be required to study all the various facets of this proposal by all the regulatory bodies concerned.

INDIA

Coal production

In 1956 the Government of India constituted a body known as the 'Coal Council of India' to study and review the present and future problems of coal production, preparation, transportation and utilization. The Coal Council in turn set up four committees to deal separately with: (*1*) assessment of coal resources and reserves, (*2*) requirements and utilization of coal, (*3*) production and preparation of coal, and (*4*) transportation, with special reference to coal.

The first committee has formulated a standard procedure for the assessment of reserves, both in quality and in quantity. The different types of reserves are classified into 'proved', 'probable', and 'inferred', and particular attention has been paid to the accurate re-assessment of reserves of coking and semi-coking types, because of the rapidly increasing demands for such coals. Based on the standard procedure, a re-assessment of the reserves of coking coals of the Jharia field has already commenced.

The second committee has reported that the major contribution to the total energy needs of India will necessarily be from coal, and they consider that the consumption of fuel in the coming years will increase rapidly, from 37 (1955) to 300 (1975) million tons coal equivalent; oil synthesis beginning about 1965 and requiring 40 million tons in 1975.

Against the production target of 60 million tons per annum to be reached in 1960, the output in 1957 was 43·5 million tons and this was an increase of about 3·5 million tons over the production of 1956. The states of West Bengal and Bihar contributed over three quarters of this total.

Part of the increased production will come from the existing mines, but new mines are also being opened up by the Government in order to achieve a target of 12 million tons per annum for the Government owned mines. As much of this production will come from mechanized open-cut mines, each yielding up to 1·5 million tons per year, a mine machinery factory is being

established in the Bengal–Bihar coalfields with an annual production capacity of about 30 to 40 thousand tons of mine machinery. In addition, a factory for heavy engineering machinery is to be set up with Russian assistance near Ranchi, Bihar.

Already the exploratory drillings for coal have shown that the country's assets of coking and non-coking coals are much greater than previously estimated.

Coal washing and coal washeries for steelworks

To meet the coking coal requirements of the three new steelworks now nearing completion and those of the existing works after expansion (Jamshedpur and Burnpur), washing of raw coking coal has been considered indispensable: approximately 9 million tons of raw coking coal per annum will be washed in central washeries. One such washery installed at Kargali (Bihar) will yield 1·5 million tons of washed coal per annum for the steelworks at Bhillai and Rourkela. The construction of the second central washery at Dugda will be undertaken shortly. It will give about 1·8 million tons of washed coal for the coke ovens at Rourkela and Bhillai. The steelworks at Durgapur (West Bengal) will have its own washery to give 1·1 million tons of washed coal per annum. Proposals have been put forward for two further central washeries, one at Bhojudih the other at Patherdih, both in the Jharia field. The washing capacity (per annum) at Bhojudih will be about 1 million tons, while Patherdih will handle about 1·5 million tons. The construction of these two central washeries is likely to be started by 1960.

Central washeries will generally consist of combinations of heavy medium washers (for plus 1 in. or plus ½ in. sizes) with jigs or cyclone washers to deal with the smalls. Of the earlier washers in operation, two are heavy medium (Chance type) with a total washing capacity of about 500 tons per hour: the other is an ACCO jig washer with feldspar bed and of capacity 75 tons per hour. A washer of the Humboldt type is being installed at Nowrozabad (M.P.) to upgrade (non-coking) coal for cement manufacture. It has a washing capacity of 120 tons per hour, and is likely to be completed soon.

The three new steelworks (each of 1 million tons ingot capacity) together with the existing steelworks (after doubling their present production capacities) will produce in all 6 million tons of ingot steel by 1960–61. Of the three new works, those at Rourkela and Bhillai have completed the construction of their coke ovens and these ovens will soon be in full production. In addition the coke ovens of the Durgapur Industries Board of the West Bengal Government will be in production by the middle of 1959, but the coke produced there (about 0·3 million tons per annum) is largely for foundry purposes; a proposal is under active consideration to supply domestic and industrial consumers with the gas, mainly through a 110 mile gas grid from Durgapur to Calcutta.

The existing steelworks at Jamshedpur and Burnpur have nearly completed their reorganization programmes: the steel output from these plants will increase substantially during 1959, and will reach 3 million tons per annum by 1960.

Power and transport

In the washing of Indian coals large quantities of middlings are inevitably produced: there is much near-gravity material and much finely disseminated shaly matter. The middlings are suitable for power generation. Accordingly, thermal power plant of over 125 MW capacity is proposed alongside the Dugda washery. Similarly, a power station of 150 MW capacity is being installed at Durgapur, while the Korba power station (at present of 90 MW capacity) is to increase its capacity to about 240 MW by the end of 1961 and utilize the middlings produced in washing the thick (100 ft) Jatraj seam.

The largest consumers of coal in India are the railways. With the increase in demand for coking coals for the steelworks, most of the coking coal used by locomotives will be diverted for the manufacture of metallurgical coke. The railways will take the better grades of non-coking coals, which occur in Bengal–Bihar; but, in order to use also the non-coking coals from the outlying fields, washeries are proposed at or near the marshalling yards.

Considering the difficulty of producing annually 100 million tons of better quality coals for the railways alone, the *1958 Report* of the Expert Committee on Railway Fuel has recommended further electrification and dieselization, so that by 1975 half of the total traffic load will be borne by electric and diesel traction. Several diesel locomotives have been put into service for goods traffic to handle the increasingly heavy train loads on various tracks.

Fertilizers and by-products

Under the programme for agricultural development, more nitrogenous fertilizer is considered indispensable. The capacity of the Sindri Factory has been expanded. Ammonium nitrate-sulphate (400 ton/day) and urea (70 ton/day) are now produced from the surplus coke oven gas available at Sindri. A fertilizer plant for 1800 ton/day of nitrolime is to be established at Rourkela alongside the works. The plant at Nangal (Punjab) will manufacture ammonium nitrate using electrolytic hydrogen along with nitrogen from liquid air plant. The fertilizer plant in Neyveli (S. Arcot) will manufacture urea (1000 ton/day) from the ammonia synthesis gas obtained by gasification of lignite. In this way, the total output of nitrogenous fertilizer will be doubled by 1960.

Plans for the manufacture of synthetic dyestuffs in partnership with Baeyers of West Germany are being finalized: the plant will be located at Bombay. Simultaneously, plant to manufacture intermediates from coal-tar bases is being projected with foreign aid. The provision of tar distillation facilities at the new steelworks will make possible the recovery of the tar bases required by the industry. It is also proposed to set up a drug factory for the manufacture of anti-tuberculosis drugs from γ-picoline.

Oil and natural gas

The amount of mineral oil products consumed annually in India is at present about 5 million tons, about 90 per cent from imported crudes processed at the refineries at Bombay and Vizagapatam. The total refinery capacity available within the country is some 4 million tons of crude per annum.

It is estimated that the total consumption of oil products by 1975 will increase seven- or eight-fold. Even at present a rising trend in the use of middle distillates is noticeable, and by 1975 kerosene and diesel oils may constitute about 65 to 70 per cent of the total oil needs of India. In order to meet a substantial part of the demand, the newly proved oilfields at Naharkatiya and Moran (Assam) will be exploited energetically: they are expected to yield 2·5 million tons per annum. Additional exploration for petroleum is in progress under the direction of the Oil and Natural Gas Commission at Jwalamukhi (Punjab), at Cambay (Saurastra), and at Baroda. Mineral oil has already been proved at Lunej near Cambay and also at Baroda, but the potentialities of these oil-bearing tracts are yet to be ascertained. Similarly, natural gas has been reported from Jwalamukhi, but the reserves again remain to be assessed. Two new oil refineries are proposed, one at Gauhati (Assam) the other at Barauni (Bihar), to process between them about 2·5 million tons per annum of Assam crude. The refinery at Digboi continues to process about 0·5 million tons per annum.

Lignite

Open-cast mining of the lignite at Neyveli in S. Arcot, Madras State, is proposed over an area of 5·4 square miles: there is an estimated reserve of 200 $\times$ 10^6 tons. The average thickness of the lignite bed is about 50 ft and the average overburden 200 ft. In the early stages the production aimed at is 3·5 million tons per annum, to be increased to about 7 million tons by 1965. Initially, about half of the lignite will be used untreated for power generation. The installed capacity of the station will be 200 MW at first, to be increased to 500 MW by 1965. There is a phased programme of development covering the production of briquettes including carbonized briquettes for domestic use and also fertilizer manufacture from gasification of the lignite. A recent proposal is to supply Madras City with gas. Laboratory facilities are available at Neyveli for studying the different processes proposed on a pilot plant scale.

Scientific research

There has been much activity in coal and oil investigations and research. In coal research, both fundamental and applied, the Central Fuel Research Institute, India, has continued to play the major part. Investigations have been carried out into the nature and constitution of coal into binderless briquetting, anomalies of surface area measurement by heat of wetting, and spontaneous combustion. Studies have also been made into the Fischer–Tropsch synthesis, gasification, carbonization, and hydrogenation.

Pilot plant work has been done on coal gasification, coal beneficiation, and carbonization. A battery of high temperature coke ovens (3 ovens of 14, 16 and 18 in. width) with complete by-product recovery came into operation in June 1957. The ovens are being utilized for tests for selection of coals and their blends for coking. Pilot scale tests on coking have also been carried out using in the blends substantial quantities of (*1*) substandard coking coals, (*2*) non-coking coals, and (*3*) LTC 'char'.

Laboratory tests have been made for guidance in proposals for washing coals from the Jharia coalfield. A semi-commercial coal-washing plant

consisting of a heavy medium separator (20 ton/h) and a jig (20 ton/h) is under construction at the Central Fuel Research Institute and will soon be in operation. Pilot plants have also been installed for low pressure briquetting (1·5 ton/h), entrained bed coal-dust gasification (50 lb/h), heavy medium cone separator (400 lb/h), heavy medium drum separator (1 ton/h), and a 6 in. cyclone washer (2 ton/h). The construction is in progress of a slagging-type gas-producer (400 lb/h), of a Koppers Totzek dust coal gasification plant (400 lb/h); of low temperature carbonization plant (20 to 30 ton/day)—externally heated, with complete by-product recovery system; of Lurgi pressure gasification plant; of plant for tar hydrogenation; and of plant for washing fine coal (10 ton/h).

ITALY

Technical meetings

Among the scientific and technical meetings held in Italy during 1958, the most important was the joint congress of Società Chimica Italiana and of the Society of Chemical Industry (Turin, 26 May to 2 June). A short résumé is given here of some of the papers submitted to Section XX 'Fuel Chemistry'.

G. COSTANTINIDES and G. ROTTERI (Istituto di Chimica Applicata, Università, Trieste) reported on a new, simple method of both evaluating the detergent capacity of unused lubricating oils and following up the behaviour of this property in use on diesel engines, irrespective of the fact that degradation may be due to oxidation phenomena or contamination by carbon black.

A. GIRELLI and C. A. FRATTA (Stazione Sperimentale per i Combustibili, Milan) presented the results of work on the structural characterization of gas oil fractions from Italian crudes (Cortemaggiore, Ragusa, and Alanno). Their composition has been compared with that of two gas oils from Aramco and Bachaquero crude oils, chosen for their characteristic structure: the first paraffinic, the second aromatic-naphthenic. The study was performed on the different gas oils, previously fractionated, with the *n–d* method.

R. RIGAMONTI, M. PANETTI and L. OLIVIERI (Istituto di Chimica Industriale, Politecnico, Turin) investigated the effects of adding substances containing the —CON , —C:NH—N , and —CS—N groups on the yields of urea adducts of hydrocarbons. Many of these substances, other conditions being equal, raise the adduct yield, while others diminish it. Results were different according to whether a pure hydrocarbon (cetane) was used or a blend thereof. The determination of molecular weight, density, refractive index and *n*-paraffins according to Leithe on the hydrocarbons separated from the Cortemaggiore crude showed that these additions also caused changes in the percentage of *n*-paraffins and the mean molecular weight of the extract obtained.

A. RIO and M. CERRONE (SAMA, Colleferro) examined maltenes obtained from natural bitumen and petroleum, their effect on the structure and properties of the bitumens which contain them, and finally the effect of the rapid transformation of maltenes by oxidative phenomena and polymerization, on the same properties.

P. M. STROCCHI and P. GANDUSIO (ENI, San Donato Milanese) presented a study on correlation of the quality of the finished products (carbon electrodes) with the type of binding tar or pitch.

Papers of interest to fuel technologists were also submitted to other sections of the congress. These included work by B. CASU and G. CAROTI (Stazione Sperimentale per i Combustibili, Milan) on the infra-red spectra of adducts of urea and urea-d_4 with straight-chain paraffinic hydrocarbons, and by G. MILAZZO *et al.* (ENI, San Donato Milanese) on vanadium determination in fuel. All the papers mentioned here have been published in *La Rivista dei Combustibili*, Nos. 6 to 10, 1958.

The Third International Meeting on Hydrocarbons took place in Piacenza from 11 to 13 September. Papers dealing with chemical utilization of natural gas, with problems connected with its utilization in the town gas industry, and in the long-distance and overseas transportation of natural gas, were submitted by authors of different countries. An exhaustive report on the meeting has appeared in *Petroleum Times*, October 1958. Complete proceedings of the meeting will be published, as usual, by the organizing committee.

The annual convention of the ATI (Italian Association of Thermotechnical Engineers) was held in Milan and Piacenza in September 1958. Papers on efficiency and economy in the production of power were discussed.

A symposium on industrial production of atomic energy was held in Milan on 12 to 14 December.

Meetings in 1959 include the 1959 session of the annual meetings on hydrocarbons (Piacenza, September) and the annual congress of the Associazione Termotecnica Italiana.

Participation of Italian scientists and technologists in the Fifth World Petroleum Congress (New York, June) includes the presentation of sixteen papers on different aspects of petroleum technology.

A French–Italian symposium on petrochemistry will be held April during the International Exhibition of Milan.

JAPAN

By invitation of the Japanese government, SOFREMINES (France) sent 15 experts to investigate the coal mining industry in Japan, and their extensive 12 volume report was published in April 1958. According to their estimate, the total energy requirement of Japan, if represented by coal of 6 500 kcal/kg, will be: 1965—190 million tons; 1970—290 million tons.

It is also estimated that it will be possible to produce 69·8 million tons of coal in 1965, and 76·5 million tons in 1970 if the coal mining industry is rationally operated.

The employment of oxygen in steelmaking has become popular among leading iron and steel companies, and it is expected that the volume of surplus coke-oven gas will be increased gradually. Its utilization as a town gas or for ammonia synthesis has already been practised to a certain extent or is under investigation.

A novel method of manufacturing town gas from pulverized non-caking coal was for the first time realized towards the end of September in Kushiro, Hokkaido, based on the experimental results of a pilot plant in the Resources Research Institute.

Petro- and gas-chemical industries are going on very actively, and many companies, some of which are newly established, have begun the manufacture of ammonia, urea, polyethylene, aromatic hydrocarbons, etc., from either natural gas or petroleum products.

In the Atomic Research Institute, reactor No. 1 (60 kW)—a water-boiler type—has been running smoothly since its installation in August 1957. Construction of reactor No. 2 (10 MW)—Type 5 Chicago pile—is now nearly complete. Another 10 MW reactor—the natural uranium fuel heavy water type and the first to be domestically produced—is planned for installation by the end of 1960.

The Japanese Petroleum Institute was founded in May 1958 with Professor Kobayashi as its first president.

The Committee for Promoting Utilization of Low Grade Coal [see *Fuel, Lond.* 1958, **37**, (No. 1), 110] issued, in June 1958, a 122 page report in which it was concluded that establishment of a coal gasification industry in Japan in her present condition of high coal price is not practicable.

Publications

AXIAL FLOW COMPRESSORS

J. H. HORLOCK. London: Butterworths Scientific Publications, 1958. *xvi* + 189 *pp.* (illus.) 40*s*

THE theory of axial flow compressors has developed enormously in the last decade, and it has drawn largely on established bodies of aerodynamic theory as well as developing along its own paths. There has been for some years a need for a book which gathers together the general aerodynamic and thermodynamic background theory, and the particular theory, of axial compressors. Dr HORLOCK is well qualified to write such a book, having been in close contact with the Compressor world for the past decade, and having himself led in the development of parts of the advanced theory.

This book has nine chapters. The first deals with background fluid mechanics and thermodynamics in the compact manner appropriate to the intended graduate reader. The further chapters deal with potential flow through cascades (and here a sound background of potential flow theory is assumed in the reader); cascade performance (including American information additional to the well-known Howell–Carter British data); 'two-dimensional' design of compressor stages; three-dimensional flow in compressor stages (Dr HORLOCK here draws largely from his own work and that of the Cambridge school); calculations of compressor performance (following Howell's methods, but including discussion of recent work on secondary flows); stalling and surging of compressors; compressor testing; and supersonic compressors. As an appendix a preliminary design study of an axial flow compressor is given.

The reviewer has no hesitation in saying that this book is a necessity for the designer, teacher, researcher and advanced student in the field of axial flow compressors. It provides an excellent bridge between the elementary treatments and the original papers, and may well become a standard text on the subject. Very full references are given to original work, and in almost all respects the data given are completely up to date.

A. G. SMITH

HANDBOOK OF THE PETROLEUM INDUSTRY

Advisory Editor: G. SELL. London: George Newnes, 1958. *viii* + 213 *pp.* 25*s*

THIS book is an attractive and very readable account of the world petroleum industry, and it reflects great credit on the authors, the editors, and the publishers alike.

Whereas it is stated in the foreword that it is not intended for the young student only, but also for those already engaged in the industry, it is none the less quite fair to judge it by its suitability in the former context. On this basis there are points of valid criticism.

It is difficult, in telling certain stories, to decide where best to begin; and this applies particularly to the story of oil.

Section 1 of this book makes a rather heavy start, with the almost immediate introduction of various technical concepts and terms, such as the migration of hydrocarbons, porosity, permeability, darcys, centipoises, and a number of geological terms, which might dull the interest of many a reader at the very outset.

There is a technique commonly used in the film industry known as the 'flash-back', in which early causative events are recalled to illuminate a current situation. Such a technique would seem to find an ideal application here. Surely it would have been better to start by describing crude oil (and at once dispelling the still widely held notion that London's 'buses run on it), pointing out its cocktail character and giving a simple account of its general hydrocarbon composition, and then to go back to origins and sources, preferably in a gentler and more lucid style than that of Section 1.

As an alternative Sections 1 and 2 might with advantage be transposed to give a smoother start to the story, and incidentally a truer one, in the sense that oil was found at the earth's surface ages before it was discovered that it existed deep underground and could be won by drilling.

Incidentally, it is also felt that the mention in Section 1 of the association of oil finds with igneous and metamorphic formations, so very rare, could be omitted in the interests of simplification, and replaced by a descriptive reference to salt domes, which are not mentioned until Section 3 on page 31, and which are found in such vast size in the Middle East in association with considerable oil reservoirs.

Section 6 gives a concise and imaginatively written account of distribution problems, emphasizing the general resourcefulness and flexibility characteristic of the operational departments of the principal oil companies of the world.

Apart from a superfluous comma in line 22 on page 41, the book is singularly free from errors.

The charts and table which are within Section 15 might be more clearly identified in the relevant text, and it would seeem that the table should have preceded the charts in order.

There are three items which might be considered for inclusion in future editions: (*1*) A brief section on elementary hydrocarbon chemistry, dealing with simple paraffins, naphthenes and aromatics, with some mention of isomers; (*2*) A brief bibliography for the benefit of those readers who may wish for further information; and (*3*) A reference to the considerable library of oil industry films, available generally from the Petroleum Films Bureau.

J. R. JOYCE

CHEMICAL ENGINEERING PRACTICE

Volume V. Fluid Systems I

Edited by H. W. CREMER and T. DAVIES. London: Butterworths Scientific Publications; New York: Academic Press, 1958. *vi* + 695 + *xxiv pp.* (illus.) 95*s* or $13.30

Chemical Engineering Practice Volume V is a text that can be divided into three major sections. Section 1 is on the transportation of fluids and contains contributions from a number of practising engineers of I.C.I. Ltd, Billingham and Edwards High Vacuum Ltd. Section 2 is a single chapter by Professor D. M. NEWITT and Dr K. E. BETTS of the Imperial College of Science and Technology on the design of high pressure vessels, whilst the third is a group of chapters on liquid–liquid extraction and distillation by Professors F. H. GARNER and S. R. M. ELLIS and members of the Birmingham University Chemical Engineering Department.

The chapters on the transportation of fluids are generally practical in their treatment, as is evidenced from the manner in which many of the relevant equations have been simplified by grouping together terms of known numerical value into one constant. This practice is very convenient to the frequent user, but is one that could irritate an enquiring reader.

Chapter 1 by W. HEY deals with chemical works pumping. It is concise and continually refers to chemical works practice. However, proportioning pumps could have been treated in a little more detail and a bibliography would have inspired further reading.

The second chapter by W. R. BARRETT, J. JACKSON and J. BROWN is entitled 'Fans, Blowers and Compressors' and gives a complete description of the various machines in use in the chemical industry. The paragraphs on 'starting up' procedures and the compression of toxic and inflammable gases, together with the fault finding chart on page 132 emphasize that these authors have had considerable practical experience. The theoretical treatment is, however, standard, yet every opportunity has been taken to illustrate the theory with worked examples. The chapter is supported by 24 references.

Chapter 3 by G. J. WILLIAMSON on 'Pipe Systems for Liquids and Gases' covers most aspects of industrial piping ranging from the physical and mechanical properties of constructional material to suitable methods of heating and insulating pipelines. Topics such as thermal expansion allowance, reaction forces in pipe bend supports, etc., are concisely but

adequately treated. The treatment of pressure drop in pipes and fittings is brief but has already been dealt with in Volume IV of this series. Most of the references are to British Standard Specifications.

Chapter 4 on the 'Design of Pressure Vessels' contrasts greatly with the previous chapters, in that the subject is treated theoretically. Equations are derived for safe thicknesses of single layer, compound and multilayer vessels, and the deductions made are supported by experimental results usually presented graphically. It is a great pity that this chapter unlike most of the others in the book does not contain a worked example to demonstrate the use of the design equations given.

Chapter 5 on the production of vacuum gives a somewhat disjointed account of vacuum pumps and their ancillaries. Some paragraphs are laboriously long and contain unnecessary statements, such as for example 'the ratio of the product of the flow velocity fluid density and pipe diameter to the fluid viscosity', which could have been replaced by 'Reynolds No.' without loss of clarity. Phrases such as this, and the fact that *Figure 34* is similar to *Figure 1* of Chapter 4 again suggest poor editing. This chapter, however, contains two very instructive examples and 23 references are given.

The final section of six chapters is concerned with liquid extraction and distillation. Chapter 6 is on liquid–liquid equilibria and is mainly devoted to the representation, and to the methods of determination, of three component liquid phase equilibria. Chapter 7 presents clearly most of the established methods of liquid phase stagewise analysis and additional methods which to date have only appeared in scientific journals. The new methods are illustrated by examples. Chapter 8 discusses the type of equipment used in industry and in the laboratory for solvent extraction processes and some indication is given of the capacity of these different units.

Chapters 9, 10, 11 and 12 give a complete treatment of fractional distillation. Chapter 9 on vapour–liquid equilibria has been well thought out and is clearly presented. Chapter 10 on the rectification of binary mixtures is equally well presented, including an introduction to batch rectification analysis when hold-up is present. Chapter 11 gives a full treatment of multicomponent continuous distillation processes, when the components do not form complexes. Extractive and azeotropic distillation processes are described, but are not analysed. Chapter 12 considers the capacities of different types of distillation equipment from the point of view of plate pressure drop, plate spacing, etc. Throughout this section, example calculations are given to demonstrate the theory and each chapter is supported by a valuable list of references.

This volume should prove a most useful addition to our chemical engineering literature.

G. V. JEFFREYS

NOMENCLATURE OF ORGANIC CHEMISTRY 1957

International Union of Pure and Applied Chemistry: Butterworths Scientific Publications; London, 1958. *v* + 92 *pp.* 15*s*

IN the early days of organic chemistry newly discovered substances were commonly given trivial names that referred to the natural product from which they were derived, or to some accidental relation to another compound (for example pyrogallol, nicotine and nicotinic acid, mesitylene and mesityl oxide). Since only one or two of a set of isomers might be derived from any one natural product it sometimes happened that closely related substances eventually received quite different names, e.g. hemimellitene, pseudocumene and mesitylene for the three trimethylbenzenes. As the number of known organic compounds increased and sets of isomers became more completely explored, a greater need was felt for systematic nomenclature. Such nomenclature should have the property of distinguishing clearly between members of a set of related compounds while at the same time demonstrating the nature of the relationship. Thus a compound's name should show as simply as possible what its structure is, because its structure is the key to its properties.

The system of nomenclature now in general use is based on recommendations made by an international conference in Geneva in 1892. These were revised and extended in 1930,

1936 and 1938. By 1947 further revision was felt to be necessary, and the book reviewed here is the result.

The book contains a set of definitive rules for the naming of all classes of hydrocarbons and of heterocyclic systems. The rules deal, *inter alia*, with the numbering of substituents, the naming of condensed cyclic systems and the setting out of their structural formulae in in print, and the naming of radicals. The naming of substituents other than hydrocarbon radicals is unfortunately not dealt with: a comprehensive guide to organic nomenclature must await the publication of further rules. The object of the drafting Commission was to codify existing practice rather than originate new nomenclature. Consequently none of the rules is of a novelty likely to offend the conservatively-minded, and indeed the whole set should gain general acceptance. The nomenclature adopted by the Chemical Society in its publications in fact conforms closely to the IUPAC rules, and still closer conformity is being considered. It is clearly desirable that other publishing bodies should also ensure that their practice corresponds to a standard system.

The present book probably covers 60 to 70 per cent of the problems that arise in naming organic compounds. The rules in it are clearly expressed and well furnished with examples. The average chemist glancing through the book may wonder a little at the fineness of detail the Commission has felt necessary to consider. Does it really matter which way round the structural formula for pyrene is set out? In fact it does matter, for if a single rule for setting out polycyclic structures is followed systematically, then a second rule gives uniquely the system of numbering substituent groups. Memorizing the rules then takes the place of remembering innumerable individual cases. In the past different numbering conventions have been used for polycyclic systems in German, British and American literature, with confusing results. Therefore study of this little book is recommended to all organic chemists, not merely to help them achieve standard practice in their publications, but also to make familiarity with their subject easier to maintain.

The lay-out and printing of the book are excellent.

P. H. GIVEN

Letters to the Editor

Letters to the Editor on points of scientific interest related to fuel science are invited. The Editor does not hold himself responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.

Chemical Structure of Coal (1)

IN A recent article[1] in this journal Dr I. G. C. DRYDEN makes an admirable attempt at checking the self-consistency of the various methods now available for the constitutional analysis of coal. After careful study of his exposition I should like to make the following remarks.

The first concerns the distinct preference Dryden shows for the results of *x-ray diffraction*, *infra-red spectroscopy* and *nuclear magnetic resonance* over those of the methods based on *molecular volume* and *molecular refraction*. In may opinion this preference is unwarranted as yet.

Taking the most recent x-ray examinations by R. DIAMOND[2] as a starting point, it is evident that far-reaching information is derived from a relatively small part of the diffraction curve which, moreover, shows only very slightly marked intensity maxima. For this reason the accuracy of the method should certainly not be overestimated. The data based on *infra-red spectroscopy* require knowledge of the constant

$$\frac{H_{ar}/H_{al+alic}}{D_{3030}/D_{2920}} = C$$

From measurements on model substances[3] it has appeared that the value of this constant lies between 1 and 3; Dryden himself, when interpreting coal constitution, suggests[1] that this value may be as high as 4. The constant C may be dependent on structure. In the extreme cases ($C = 1$ or 4) this causes differences in the structural parameters C_{ar} and R_{ar} which may exceed 100 per cent. The data derived from *nuclear magnetic resonance* must as yet be considered inaccurate, for the method of calculation is based on a very limited number of model substances one of which gives large deviations[4].

However, be it clearly understood: I warmly acclaim these new methods, which are all being studied at my laboratory. I only wish to warn against a premature overrating of their significance.

My second remark concerns Dryden's statement (ref. 1, page 446): 'Van Krevelen . . . has claimed incorrectly that the omission of B/C' gives average values of the other parameters of the whole molecule; but on the contrary, it gives meaningless values'.

First, I wish to point out that this is an incorrect quotation. Actually, the challenged passage reads: 'If B/C' cannot be determined, or if it is not possible to prove that B/C' is negligibly small compared with the ring condensation index, the calculation *of the latter* (i.e. the ring condensation index) yields a value which is to be considered only as an average for the *whole* molecule'[5].

No mention is made here of 'the other parameters'. The aromaticity, for instance, is the same for the whole molecule and for the structural unit. Furthermore, the values thus found are certainly not meaningless. I am fully prepared to demonstrate this again.

The relationship

$$H' = (2C' + 2) - 2R - C'_{ar} \quad \ldots . [1]$$

which can be easily reduced to

$$[2 - f_a - H'/C'] = 2\,(R - 1)/C' \quad \ldots . [2]$$

is valid, *without any restriction*, for all organic C, H and O-containing molecules that are free of olefinic double bonds, triple bonds and O=C-bonds*). *It holds for the molecule as a whole* (even if polymeric). This proves that the ring condensation index, which can be experimentally determined as the quantity $[2 - f_a - H'/C']$, *is indeed useful as a value averaged over the whole molecule, even when this has a very complicated structure.*

The question: 'Does this quantity also provide information on the average structural unit, the average ring cluster, in coal?' must be answered in the affirmative. For the structural unit may, in analogy with equation 1, be represented as

$$H'_u = (2\,C'_u + 2) - 2\,R_u - C'_{aru} - 2\,b \quad \ldots . [3]$$

or

$$[2 - f_a - H'_u/C'_u] = 2\,(R_u - 1 + b)/C'_u \quad \ldots . [4]$$

where b is the number of bridges per average structural unit. If the molecule consists of m structural units, linked by bm bridges and the bridge bonds form rm extra rings, the following equation[6] is valid

$$b = (m - 1)/m + r \quad \ldots . [5]$$

Substitution gives

$$[2 - f_a - H'_u/C'_u] = 2\,(R_u + r - 1/m)/C'_u \quad \ldots . [6]$$

Since $R_u + r = R_{u(total)}$, while furthermore $1/m$ very rapidly decreases to a value much lower than $R_{u(total)}$ (with $R_u = 3$ and $m = 2$, the ratio is already 1:6) we may say that by approximation

$$[2 - f_a - H'/C'] \approx 2\,R'_{u(total)}/C'_u \quad \ldots . [7]$$

in other words, the experimentally accessible quantity $[2 - f_a - H/C]$ *indeed also gives a measure of the average number of rings per average structural unit.*

My third remark bears upon Dryden's method itself. To permit its application he assumes:

(*a*) $B = 2$

(*b*) a correction term $\frac{1}{2}\,(1\text{–}f_a\text{–}f)$ for the alicyclic rings

(*c*) $H'_{alic}/C'_{alic} = 2$.

* For the latter a correction can be made, provided the content (of O=) is known.

Assumption (*a*), if applied to the whole range of rank, is disputable. Assumption (*b*) implies that four alicyclic carbon atoms always replace one aromatic hydrogen atom. This assumption is, as far as I can see, not compatible with assumption (*c*).

I have the impression that Dryden, by making these three assumptions, introduces structural elements and deprives his method of its validity as a really objective test. The formula which Dryden gives for (*b*), viz.

$$B = 2\,l\,(m - 1)/m \qquad \ldots . [8]$$

is in my opinion incorrect (although this has no repercussions on his conclusions since he uses the value $B = 2$ in his article). In conclusion, I wish to make one more remark. In this article Dryden points to the *discrepancies* between the results obtained with the various methods. I, on my side, would rather draw attention to the fact that ten years ago not a single method was available for determining, say, the aromaticity of coal, while Dryden is now able to mention six such methods (to which I could add one more, viz. the method based on sound velocity[7]). These yield values which, though not identical, are at this stage already reasonably well in line with each other as appears from the data cited by Dryden.

Coal	1	2	3	4	5
C%	82·5	85	87·5	90·0	92·5
f_a (*extreme values of 6 methods*)	0·71–0·83	0·72–0·845	0·74–0·865	0·78–0·89	0·845–0·95

Ten years ago such a result was beyond all expectation.

I wish to thank my collaborators H. A. G. Chermin, P. M. J. Wolfs and J. Schuyer for their valuable discussions on some of the points dealt with in this letter.

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(*Received December 1958*)

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I have the following comments to make on the above letter by Professor D. W. VAN KREVELEN.

(*1*) In the paper under discussion[1], it was deduced that results from the x-ray, infra-red and n.m.r. methods could be brought into better mutual agreement than those from molecular volume, molar refraction and calorific value. This was an objective finding and not a 'preference'.

(*2*) I apologise if my original quotation[1] from the book[2] by D. W. VAN KREVELEN and J. SCHUYER was inaccurate; admittedly the ring condensation index alone was cited in the book, but since 'other parameters' such as ring number are related to this the two versions are surely almost equivalent.

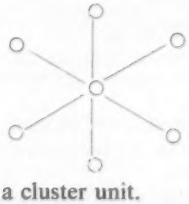
(*3*) The disagreement between van Krevelen and myself over the neglect of B/C' in equation 2 of his letter has been clarified by discussion between us. My statement that this gives, not average values of the parameters for the whole molecule (cf. *2* above) but on the contrary meaningless values, now appears a half-truth.

Equation 2 leads, it is true, to a value of $2(R–1)/C'$ for the whole molecule. When this molecule contains several clusters the value of R will be large, therefore $(R–1) \sim R$ and the parameter obtained is approximately $2R/C'$ which is equal to $2R_u/C'_u$ as in equation 7. These quantities, however, are not the same as $2(R_u–1)/C'_u$ because R'_u is small. The difference is large, sometimes 40 per cent of the value of $2R/C'$; it is equal to $2/C'$ and therefore not far from the value of B/C', if I am right in assuming that $B \sim 2$. Thus the index calculated from equation 2 yields a value corresponding to the total rings in the molecule, and from it *as it stands* little else can be deduced (hence the 'meaningless values'); but if *either* B/C' be subtracted and already published graphs[1] are used, *or* the RHS be rewritten $2R/C'$ and new graphs are set up, cluster sizes can be estimated. The value of R_u thus deduced will include closed structures formed by interlinkage of clusters, however large or loose. This clarification is satisfactory because it widens the range of the method and throws a new light on the significance of the results—and not least, appears to allow both parties to withdraw with honour!

(*4*) I agree that B may vary with rank but one cannot assume this and my point was that variation was likely to be comparatively small.

(*5*) The assumption relating aliphatic carbon atoms to aromatic hydrogen atoms was empirical[3], but seemed to hold reasonably well for model compounds. It has no relation to the ratio of alicyclic hydrogen to carbon.

(*6*) Equation 8 in the above letter was used by me to estimate the most likely range of values for B, but the value of 2·25 finally chosen depended on the experimental data analysed. The equation can be considerably in error for certain unlikely and unusual structures such as



where each circle represents a cluster unit.

(7) Regarding the agreement shown in van Krevelen's final table, one purpose of my paper was to point out that the small difference in f_a could imply a considerable difference in ring cluster size and that f_a was consequently an insensitive and perhaps misleading parameter through which to compare the results of different techniques.

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Hydrogasification of Bituminous Sand to Ethane and to Pipeline Gas

AN exploratory batch hydrogasification (thermal hydrogenolysis) test was carried out on a representative bituminous sand, to compare results with those from a large number of carbon-containing materials, such as petroleum oils, coal, lignites, oil shale and pure hydrocarbons. These have been previously hydrogasified under similar conditions, as part of a continuing research programme on development of natural gas substitutes from fossil fuels[1–5].

The experimental technique employed for the test reported herein has been described in detail in the literature[3]. Briefly, the sand and hydrogen were charged to the batch reactor at room temperature and heating was begun; a 137 minute period was required to reach 1300°F, and an additional 30

Table 1. Batch hydrogasification of bituminous sand

*Feed bituminous sand**							
Charge weight, lb			0·4133				
Organic C+H, lb			0·0500				
Feed hydrogen							
Initial pressure (at room temp.), lb/in² gauge			885				
Feed ratio							
% of stoichiometric†			100·4				
SCF/ton bit. sand			8817				
SCF/lb org. C+H			36·44				
Results							
Temperature, °F	950	1025	1075	1200	1300	1300	1300
Pressure, lb/in² gauge	2245	2335	2330	2365	2360	2270	2235
Time above room temp., min	88	99	105	122	137	147	167
Conversion of org. C+H to gas‡, wt %	9·5	36·8	51·7	79·0	91·8	94·5	95·8
Product gas yield‡, SCF/ton bit. sand	8749	8662	8338	7825	7365	7089	6978
SCF/lb org. C+H	36·16	35·80	34·46	32·34	30·44	29·30	28·84
Product gas properties							
Composition, mole %							
CO	0·6	0·6	0·8	0·9	1·1	1·0	0·8
CO_2	0·1	0·1	0·1	0·1	0·2	0·1	0·2
H_2S	—	—	0·2	0·3	0·4	0·4	0·3
H_2	95·8	83·6	74·2	50·6	28·0	14·4	7·6
CH_4	1·4	7·8	13·4	30·1	56·0	77·2	88·7
C_2H_6	0·8	3·9	6·4	15·5	13·8	6·6	2·0
C_3H_8	0·5	2·3	3·4	1·4	0·1	—	—
C_4H_{10}	0·4	1·0	0·9	0·3	—	—	—
C_5H_{12}	0·1	0·3	0·3	0·6	0·3	0·2	0·1
Higher olefins	0·3	0·4	0·3	0·2	—	—	—
Benzene	—	—	—	—	0·1	0·1	0·3
Total	100·0	100·0	100·0	100·0	100·0	100·0	100·0
Heating value, Btu/SCF	371	520	612	796	904	942	959
Specific gravity, (air = 1)	0·112	0·215	0·282	0·414	0·498	0·527	0·541

* Obtained from Canada Dept of Mines and Technical Surveys, Fuels Div. through courtesy of D. S. Montgomery; I.G.T. Lab. No. 3978—10·78 wt % C, 1·32 wt % H, 0·4 wt % water.
† Stoichiometric for complete conversion of organic C + H to methane.
‡ Calculated from observed reactor pressure and temperature, and initial reactor free volume, assuming ideal gas law.
SCF refers to standard cubic feet at 60°F, 30 inches of mercury, saturated with water vapour. Under these conditions, the ideal gas molar volume is 385·2 SCF/lb-mole.

minute period was obtained at 1300°F. Seven gas samples were removed at intervals for mass spectrometer analysis. At the close of the run, the residue sand was found to be dry and free-flowing. Operating conditions and results are presented in *Table 1*.

The same general relationships between the appearance and disappearance of the stable reaction products, as for other fossil fuels, was apparent; concentrations of butanes, propane and ethane formed during the early stages of the reaction passed successively through maxima as temperature

and time were increased. The methane concentration increased continuously after initiation of gasification reactions at about 950°F, and methane was the final product of hydrogenolysis of the organic matter charged, and the intermediate gaseous paraffin hydrocarbons. Maximum concentrations of butanes, propane and ethane were obtained at 1025°F, 1075°F and 1200°F, respectively, in general agreement with hydrogasification results for a number of other bituminous materials and hydrocarbons[2,3,5].

It was found that the reactivity of the organic matter in the bituminous sand was remarkably high for a material so deficient in hydrogen, as characterized by its high carbon/hydrogen weight ratio of 8·17. High conversions to gaseous hydrocarbons were obtained early in the course of the run, and the heating value of the gas was in excess of 900 Btu/SCF upon attainment of 1300°F. The ethane yield was also considerable for such a high carbon/hydrogen ratio material—about 10000 SCF/ton of organic C + H at 1200°F, corresponding to a 39 per cent conversion of the organic C + H to ethane. This compares favourably with the ethane yield from a Colorado oil shale (11500 SCF/ton of organic C + H and 45 per cent conversion at very similar conditions)[5]. Oil shale has been previously found to be an exceptionally good charging material for the production of ethane by hydrogasification, probably because of the kerogen structure which contains significant amounts of nitrogen and oxygen.

Although this test indicates that bituminous sands may be readily converted to high heating value fuel gases, or to crude petrochemical ethane, it does not seem likely that the vast Canadian deposits will be used for these purposes in the near future. The inaccessibility of the deposits, and the continuing availability of high quality petroleum oils which can be easily converted to pipeline gas, or to ethane, will probably be determining factors. However, these thermal hydrogenolysis results have significance in a consideration of the structure of the organic matter in bituminous sands. Investigations of other fossil fuels and related pure compounds, published and in progress, appear to bear out the usefulness of the thermal hydrogenolysis approach, and such studies are being continued at this Institute as part of its Basic Research programme.

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I

Chloroform Solubility and Coking Properties of Coals Treated with Hydrogen

FOLLOWING studies at the Fuel Research Station[1], we have recently investigated the carbonization behaviour of high-volatile bright coals previously treated with hydrogen at 400°C and 200 atm. The products differed from the untreated coals not only in their ability to form highly swollen cokes but in containing more chloroform-soluble material; more of this material, also, than was extractable from unheated coking coals. This may be compared with the relation between coking properties and increase in yield of chloroform extract on preheating, which has been found for raw and oxidized coals in the bituminous range[2,3].

Table 1. Chloroform extraction of coals[2,3]

Ref. No.	*% C d.m.f. (Parr)*	*Gray–King Coke Type*	*Chloroform extract % d.a.f.*	
			Coal	*Shock heated coal*
1	78·1	*A*	—	—
2	82·5	*B*	2·8	0·7
3	83·8	*E*	2·3	1·4
4	89·3	*G+*	0·8	8·5

Table 2. Chloroform extraction of coals treated with hydrogen

Ref. No.	*% C d.m.f. (Parr) in original coal*	*Treated coal*		
		Gray–King Coke Type	*Chloroform extract % on air dried product*	
			Raw product	*Shock heated product*
5	78·1	*G*	21·0	11·5
6	82·5	*C*	4·6	2·8
7	82·5	*G+*	23·3	19·5
8	83·8	*G*	10·4	3·1
9	83·8	*G+*	19·4	11·4
10	83·8	*G+*	—	23·3

It was clear from infra-red and chemical analyses that the structure of the chloroform-soluble part of the high-volatile coals that had been treated with hydrogen was not closely similar to that from a preheated coking coal. But on shock heating these treated coals at 400°C the structure of the subsequent extract became more similar to that of the extract from a preheated coking coal. The behaviour of the coals treated in hydrogen differed from that of the untreated coking coal since, on shock heating, the high extract yields from the treated coals, in general, decreased somewhat, whereas the yield from the coking coal increased from 0·8 to 8·5 per cent[2,3].

The extraction results for the raw coals are given in *Table 1*, and for the coals treated with hydrogen in *Table 2*.

We would like to thank Dr J. K. Brown and R. Bent for determining the infra-red spectra, and A. E. Gibbs (vacation student) for preparing the chloroform extracts.

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Active Hydrogens in Coal

DEGRADATIVE chemical evidence, X-ray diffraction studies and structural analysis have provided us with a picture of the carbon skeleton of the coal species. However, our knowledge of the pattern of hydrogen distribution in coal, though equally important, is relatively less advanced. Hydrogen atoms with a partial ionic character are the most active in substitution, oxidation and all protolytic chemical reactions. A knowledge of these 'active' hydrogens in any molecule is therefore of particular interest.

Deuterium exchange permits a ready estimation of the active hydrogens in any species, since under mildly acidic or alkaline conditions the aliphatic or aromatic hydrogens are resistant to it, whereas equilibration of deuterium atoms with ionic hydrogens is rapid. It is possible to deuterate selectively, though completely, the active hydrogens in any molecule by base-catalysed successive equilibration with heavy water, resulting in progressive enrichment of deuterium. The heavy hydrogen content of the deuterated product is determined by combustion of the deuterated material and measurement of the density of the resulting heavy water. The procedure takes advantage of the appreciable difference in densities for H_2O and D_2O ($d_4^{25^\circ}{}_{(D_2O)} = 1{\cdot}1059$) and is sufficiently sensitive to make possible the estimation of small amounts of deuterium in an organic compound.

This investigation reports a value for the active hydrogens in a sample of coal from the Raniganj field, as determined by deuteration studies.

A sample of Jambad Bhowlah coal (C, 81·3; H, 5·36; N, 1·85; S, 0·4 per cent) was selected for the purpose. Anhydrous sodium carbonate was used as the catalyst for the deuteration procedure. A mixture of a thoroughly dried sample of the finely powdered coal, sodium carbonate and deuterium oxide (purity, 99·5 mole per cent) was refluxed for a day, at the end of which period, the deuterium oxide was distilled off. The mixture of residual coal and the base catalyst was refluxed with a second lot of deuterium oxide for a few hours, and this process of progressive enrichment by exchange was repeated several times. The resulting alkaline suspension of deuterated coal was neutralized by the addition of a solution of monodeuteroacetic acid and deuterium chloride prepared by the addition of acetyl chloride to heavy water. The solution was filtered, and the residue consisting of deuterated coal was repeatedly washed with deuterium oxide and dried. The deuterated sample was burnt in a combustion train and the resulting heavy water collected in a U-tube cooled in salt–ice mixture. The density of the water of combustion was determined with a semi-micro pyknometer in a thermostated room at 20°C.

The observed value of 1·007 for the density of the water of combustion corresponds to a hydrogen/deuterium ratio of 11 : 1 in the deuterated coal: the percentage of active hydrogen thus works out to 8·3 of the total hydrogen content.

Investigations are in progress to study the variation of active hydrogen content with rank and to obtain a breakdown of the active hydrogens as

hydroxylic and methylene or methyls activated by proximity to a carbonyl group.

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Dehydrogenation and Aromaticity of Coal

B. K. MAZUMDAR, S. K. CHAKRABARTTY and A. LAHIRI [*Fuel, Lond.* 1959, **38**, 115] have criticized the estimation made by van Krevelen and co-workers as to the aromatic character of coal pitch and, hence, their findings concerning the aromaticity of coal.

Lahiri and co-workers base their criticism on the results of dehydrogenation experiments with sulphur, which, they believe, provide a measure of the amount of hydrogen present in alicyclic configurations. We had, for a long time already, been doubtful of the value of this method and, for this reason, have now performed a number of experiments in which fully aromatic substances of known constitution were heated with sulphur for one hour (weight ratio—2 : 1).

All of these compounds were found to yield hydrogen sulphide (see *Table 1*).

Table 1

Compound	*Temperature at which H_2S formation starts °C*	*Dehydrogenation temperature °C*	*Percentage of original hydrogen converted to H_2S*
Anthracene	210	250 *to* 300	20
Phenanthrene	265	290 *to* 300	20
Chrysene	240	300	17
Pyrene	200	290 *to* 300	16
β-Naphthol	200	290 *to* 300	23

In the light of these findings we have to reject Lahiri's criticism as well as the aromaticity values published by this author.

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The Variation with Temperature of the Catalytic Activity of an Oxidized Stainless Steel Surface in the Oxidation of Sulphur Dioxide

THE presence of small proportions of sulphur trioxide (of the order of several p.p.m. by volume) in the flue gases of power station boilers is believed to be a prime cause of air heater corrosion. Conflicting views have been expressed[1,2] concerning the catalytic action of the superheater metal surfaces in the oxidation of sulphur dioxide to sulphur trioxide in the gases from the combustion chamber. As part of a programme of studies into the corrosion of superheater and air heater materials, a laboratory investigation was made of the catalytic effect of a potential superheater steel at temperatures likely to be encountered in boiler operation. This note presents the results of the initial experiments.

In this work a tubular specimen, $\frac{3}{8}$ in. o.d., 18 s.w.g., of F.D.P. quality (Cr, 18; Ni, 8; Ti 0·5 per cent) was used. This had been exposed to flue gas in a power station boiler and had an oxidized surface. Sulphur dioxide from a syphon was introduced via a capillary flowmeter into a stream of air entering the specimen tube, which was heated for a length of about 18 in. in a horizontal electric tube furnace. The temperature of the metal was measured with a

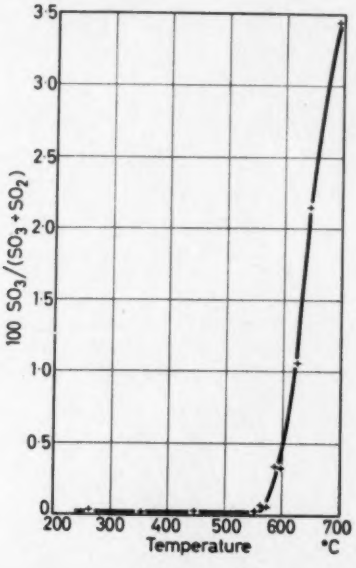

Figure 1. Relation between percentage oxidation of sulphur dioxide and specimen temperature

stainless-steel-sheathed chromel–alumel thermocouple placed inside the specimen in the middle of the heated zone. The temperature over the middle 13 in. of the furnace varied by not more than ± 5 °C from that recorded by the thermocouple. The gas exit end of the specimen tube, projecting about 4 in. from the furnace, was connected by a metal–glass spherical joint to a gas

analysis apparatus[3], and was heated electrically to about 250°C to prevent premature condensation of sulphuric acid. The concentration of sulphur dioxide was kept at 2000 p.p.m., a figure typical of flue gas derived from high sulphur fuels. Air at ambient temperature was drawn by the gas analysis apparatus through the specimen tube at about 1·0 litre/min giving a residence time of 0·7 sec in the middle 13 in. The concentrations of sulphur dioxide and sulphur trioxide in the exit gas were determined for various temperatures of the specimen tube metal. The sulphur trioxide found was expressed as a percentage of the total sulphur oxides; the results are shown in *Figure 1*.

The percentage oxidation of sulphur dioxide increased steeply as the temperature exceeded about 570°C (1058°F). We suggest that this sudden increase in sulphur trioxide formation could be due to a change in the nature of the oxide layer on the surface of the specimen. The phase wüstite, which corresponds in composition to ferrous oxide with a small deficiency of iron ions[4], is present only at temperatures exceeding 570°C[5]; its presence has been associated with an increased rate of oxidation of iron[6].

Further work is being carried out to determine the effects on this catalysis of the composition of the tube material, the oxygen concentration, and the nature of the oxidized metal surface, which may be affected by its history. The relationship between the rate of oxidation of various ferrous alloys and their catalytic activity in the oxidation of sulphur dioxide is also under investigation.

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PAPERS ACCEPTED FOR FUTURE PUBLICATION

The following papers have been accepted for publication in future issues of FUEL

THE KINETICS OF THE SORPTION OF METHANOL ON CELLULOSE. *P. Fugassi and G. Ostapchenko*

SORPTION OF POLAR VAPOURS ON SWELLING GELS. *P. Fugassi and G. Ostapchenko*

THE DETERMINATION OF PHOSPHORUS IN COAL ASH. *R. J. Cosstick and H. N. S. Schafer*

DETERMINATIONS OF HYDROXYL GROUPS IN MODEL COMPOUNDS, COAL AND COAL EXTRACTS. *A. Halleux, S. Delavarene and H. Tschamler*

EXTRACTION EXPERIMENTS ON COAL WITH VARIOUS PYRIDINE BASES. *A. Halleux and H. Tschamler*

THE INORGANIC CONSTITUENTS IN AUSTRALIAN COALS I—THE DIRECT DETERMINATION OF THE TOTAL MINERAL MATTER CONTENT. *H. R. Brown, R. A. Durie and H. N. S. Schafer*

ANALYSIS OF LIQUID PRODUCTS FROM COAL HYDROGENATION BY MASS SPECTROMETRY: USE OF RHENIUM FILAMENTS AND LOW IONIZING VOLTAGE. *A. G. Sharkey, Jr, G. Wood, J. L. Schultz, I. Wender and R. A. Friedel*

ELECTRON RESONANCE STUDY OF THE FREE RADICALS PRODUCED BY ELECTROLYSIS OF SOLVENT EXTRACTS OF A COAL. *D. E. G. Austen, P. H. Given, D. J. E. Ingram and M. E. Peover*

EFFECT OF FERROCENE ON CARBON FORMATION FROM ACETYLENE. *J. D. Frazee and R. C. Anderson*

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